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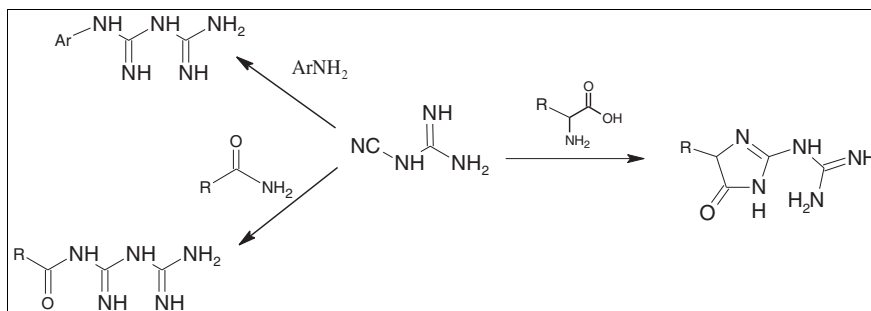
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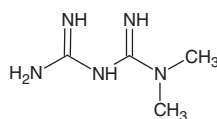


Reaction of dicyandiamide with series of amino acids afforded guanidiny pyrazolones **2–19**, respectively. Although reaction of dicyandiamide with urea, acetamide, bezamide, allantoin, *p*-aminobenzoic acid, sulphanilic acid, and adenine gave biguanides **20–26**, respectively. All compounds have been characterized on the basis of IR and ¹H-NMR.

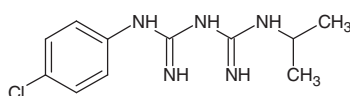
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INTRODUCTION

Diabetes mellitus is one of the most prevalent chronic diseases worldwide [1]. During the last 20 years, the total number of people with diabetes has risen from 30 to 230 million according to the International Diabetes Federation [2]. Biguanidines and cyclic guanidines are one of most active diabetic inhibitors. Metformin (sold as Glucophage) is the first line medicine used by clinicians to treat diabetic and prediabetic patients [3,4].



Metformin



Proguanil

Such guanidine-like compounds showed not only a crucial antidiabetic drugs, but also it showed a diverse of chemical, biochemical, and pharmacological properties. Recent achievements in the synthesis of guanidine-containing molecules make them of great importance to the design and development of novel drugs acting as anti-inflammatory agents, antithrombotic, and chemotherapeutic agents [5]. Guanidines showed a wide range of biological activities. For example, it not only lowers blood glucose [6] and inhibits dihydrofolate reductase of opportunistic microorganisms [7] but also acts as an anti-inflammatory [8] and fire retardant [9] (e.g., Proguanil). It is also used to develop novel drugs acting at central nervous system [10]. Synthesis of biguanidines

and guanidine-containing compounds has received intensive studies since mid of last century. Polymerisation, solvation, and high hydrophilicity [11–13] of guanidinium compounds are the main obstacles in synthesis of such compounds. Also, many of biguanide compounds have been reported in patients with obscure synthetic methods. Moreover, the whole world now gets more alert towards the global environmental chemical pollutions. Organic reactions under aqueous conditions have increasingly attracted chemists' interests, particularly from the viewpoint of green chemistry [14–20]. These values and facts prompted us to explore a simple, straightforward, and environment-friendly method of preparation of different classes of guanidine-like compounds in a good yield by using aqueous medium reaction conditions.

RESULTS AND DISCUSSION

On the reaction of dicyandiamide (DCD) with amino acids L-tryptophan, L-histidine, L-phenylalanine, L-proline, thioproline, β-alanine, D-alanine, DL-aspartic acid, isoleucine, L-threonine, L-valine, L-glutamic acid, DL-serine, L-asparagine, L-glutamine, L-arginine, L-lysine, and L-citrulline in aqueous sulphuric acid medium afforded the guanidiny pyrazolones **2–19**, respectively (Scheme 1). All compounds **2–19** were also prepared via another condition by using aqueous hydrochloric acid medium [21] instead of aqueous sulphuric acid [22]. The reaction mechanism of formation of compounds **2–19** was preceded via a nucleophilic addition of the amino group to the cyano group, then elimination of water molecule.

Chemical reaction scheme showing the synthesis of 19 triazoloindole derivatives (2-19) from 1,2,4-triazole-5-carbonitrile (1) and various amino acids. The reaction conditions are 10% H₂SO₄ or HCl. The products are numbered 2 through 19.

Starting material 1: N#CC1=NC=NC=C1

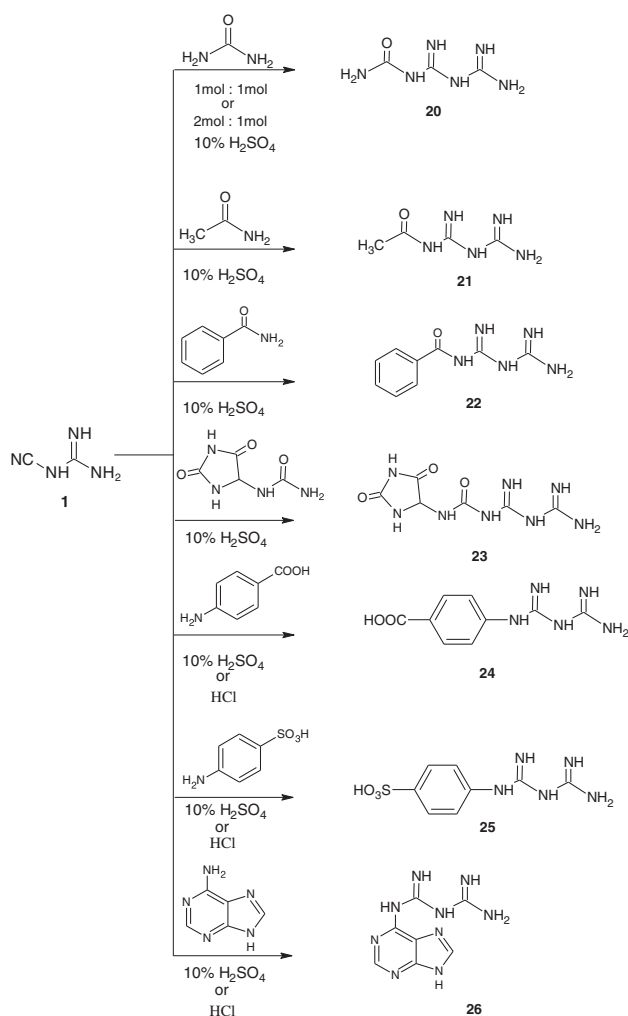
Reagents: 10% H₂SO₄ or HCl

Products:

- 2: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 3: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 4: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 5: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 6: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 7: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 8: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 9: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 10: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 11: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 12: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 13: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 14: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 15: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 16: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 17: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 18: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N
- 19: N#CC1=NC=NC=C1C1=CC=C2C(=C1)C(=CN2)C(=O)N

Dicyandiamide was subjected to react with *p*-aminobenzoic acid, sulphanilic acid, and adenine gave 4-(carbamimidoylcarbamimidamido)benzoic acid (**24**), 4-(carbamimidoylcarbamimidamido)benzenesulfonic acid (**25**), and *N*-9*H*-purin-6-ylimidodicarbonimidic diamide (**26**), respectively (Scheme 2).

Scheme 2



The reaction mechanism of compounds 20–26 was preceded via a nucleophilic addition of the amino group to the cyano group.

EXPERIMENTAL

All melting points are uncorrected and were recorded on Melt-Temp II melting point apparatus. IR spectra were measured as KBr pellets on a Shimadzu DR-8001 spectrometer. ¹H and ¹³C-NMR spectra were recorded on a Varian Gemini at 400 MHz using TMS as an internal reference and DMSO-d₆ as a solvent. Mass spectra were performed on a Shimadzu GCMS-QP 1000 mass spectrometer at 70 eV. The elemental analyses were carried out on a Perkin-Elmer 240C Microanalyzer. All compounds were checked for their purity on TLC plates.

General procedure for preparation of compounds 2–26.

Method A. L-Tryptophan, L-histidine, L-phenylalanine, L-proline, thioproline, β-alanine, D-alanine, DL-aspartic acid, isoleucine, L-threonine, L-valine, L-glutamic acid, DL-serine, L-asparagine, L-glutamine, L-arginine, L-lysine, L-citrulline, urea, acetamide, bezamide, allantion, *p*-aminobenzoic acid, sulphanilic acid, and

adenine (50 mmol) was dissolved on heating in 50 mL of 10% sulfuric acid, and DCD (75 mmol) was added. The reaction mixture was heated for 20 min, and then, 10 mL of 50% sodium hydroxide solution was added. After heating for additional 15 min, the reaction mixture was cooled; the solid collected by filtration and washed with water. The prepared compounds were sufficiently pure and were used without further purification. Recrystallised samples have been prepared for analyses.

Method B. A mixture of L-tryptophan, L-histidine, L-phenylalanine, L-proline, thioproline, β-alanine, D-alanine, DL-aspartic acid, isoleucine, L-threonine, L-valine, L-glutamic acid, DL-serine, L-asparagine, L-glutamine, L-arginine, L-lysine and L-citrulline (1 mol), DCD (1 mol), concentrated hydrochloric acid (2 mol), and water (15 cc) was heated under reflux for 3 h. The reaction mixture was allowed to cool down. Samples of products have been recrystallised from an appropriate solvent for all analysis purposes.

Synthesis of 1-[4-(1H-indol-3-ylmethyl)-5-oxo-4,5-dihydro-1H-imidazol-2-yl]guanidine 2. Yield 67%, mp 310°C; IR (potassium bromide): cm⁻¹ 3392, 3274, 3212, 3120 (4NH, NH₂), 1679 (C=O); ¹H-NMR: δ 10.30 (s, 1H, NH), 9.20 (s, 2H, 2NH), 7.92 (s, 1H, NH), 7.88–7.20 (m, 4H, arom), 6.77 (s, 1H, CH), 6.10 (t, 1H, CH), 5.50 (br, 4H, 2NH₂), 2.46 (d, 2H, CH₂); MS *m/z* (%): M⁺ 270 (20.00), 204 (33.10), 185 (11.00), 159 (09.70), 130 (100), 77 (22.30). *Anal.* Calcd for C₁₃H₁₄N₆O (270.29): C, 57.77; H, 5.22; N, 31.09. Found: C, 57.98; H, 5.02; N, 30.94.

Synthesis of 1-[5-oxo-4-(1H-pyrrol-3-ylmethyl)-4,5-dihydro-1H-imidazol-2-yl]guanidine 3. Yield 81%, mp 263–265°C; IR (potassium bromide): cm⁻¹ 3408, 3374, 3245, 3183 (4NH, NH₂), 1705 (C=O); ¹H-NMR: δ 10.00 (s, 1H, NH), 9.25 (s, 2H, 2NH), 7.80 (s, 1H, NH), 7.70–7.15 (m, 3H, Pyrrol), 6.80 (t, 1H, CH), 5.50 (br, 2H, NH₂), 2.65 (d, 2H, CH₂); *Anal.* Calcd for C₉H₁₂N₆O (220.23): C, 49.08; H, 5.49; N, 38.16. Found: C, 49.35; H, 5.34; N, 38.01.

Synthesis of 1-(4-benzyl-5-oxo-4,5-dihydro-1H-imidazol-2-yl)guanidine 4. Yield 72%, mp 305°C; IR (potassium bromide): cm⁻¹ 3420, 3366, 3226, 3183 (3NH, NH₂), 1666 (C=O); ¹H-NMR: δ 10.12 (s, 1H, NH), 9.25 (s, 2H, 2NH), 7.24–6.86 (m, 5H, arom), 6.56 (t, 1H, CH), 5.64 (br, 2H, NH₂), 2.68 (d, 2H, CH₂); *Anal.* Calcd for C₁₁H₁₃N₅O (231.26): C, 57.13; H, 5.67; N, 30.28. Found: C, 57.31; H, 5.33; N, 30.10.

Synthesis of 1-(1-oxo-5,6,7,7a-tetrahydro-1H-pyrrolo[1,2-*c*]imidazol-3-yl)guanidine 5. Yield 88%, mp >340°C; IR (potassium bromide): cm⁻¹ 3381, 3222, 3173 (2NH, NH₂), 1667 (C=O); ¹H-NMR: δ 10.08 (s, 1H, NH), 9.12 (s, 1H, NH), 6.66 (s, 1H, CH), 5.37 (br, 2H, NH₂), 3.17 (t, 2H, CH₂), 2.67 (m, 2H, CH₂), 1.59 (m, 2H, CH₂); *Anal.* Calcd for C₇H₁₁N₅O (181.20): C, 46.40; H, 6.12; N, 38.65. Found: C, 46.61; H, 5.98; N, 38.34.

Synthesis of 1-(7-oxo-7,7a-dihydro-1H-imidazo[1,5-*c*][1,3]thiazol-5-yl)guanidine 6. Yield 74%, mp 320°C; IR (potassium bromide): cm⁻¹ 3388, 3227, 3181 (2NH, NH₂), 1670 (C=O); ¹H-NMR: δ 10.05 (s, 1H, NH), 9.24 (s, 1H, NH), 6.34 (t, 1H, CH), 5.85 (br, 2H, NH₂), 4.96 (s, 2H, CH₂), 3.54 (d, 2H, CH₂); *Anal.* Calcd for C₆H₉N₅OS (199.23): C, 36.17; H, 4.55; N, 35.15; S, 16.09. Found: C, 36.19; H, 4.61; N, 34.99; S, 15.97.

Synthesis of 1-(4-oxo-1,4,5,6-tetrahydropyrimidin-2-yl)guanidine 7. Yield 76%, mp 229°C; IR (potassium bromide): cm⁻¹ 3384, 3220, 3189 (3NH, NH₂), 1681 (C=O); ¹H-NMR: δ 9.27 (s, 1H, NH), 8.45 (s, 2H, 2NH), 5.65 (br, 2H, NH₂), 3.44 (t, 2H, CH₂), 2.65 (t, 2H,

CH₂); *Anal.* Calcd for C₅H₉N₅O (155.16): C, 38.70; H, 5.85; N, 45.14. Found: C, 38.78; H, 5.77; N, 45.02.

Synthesis of 1-(5-methyl-4-oxo-4,5-dihydro-1H-imidazol-2-yl)guanidine 8. Yield 80%, mp 330°C; IR (potassium bromide): cm⁻¹ 3380, 3222, 3189 (3NH, NH₂), 1675 (C=O); ¹H-NMR: δ 9.11 (s, 1H, NH), 8.84 (s, 2H, 2NH), 5.65 (br, 2H, NH₂), 5.12 (q, 1H, CH), 1.98 (d, 3H, CH₃); *Anal.* Calcd for C₅H₉N₅O (155.16): C, 38.70; H, 5.85; N, 45.14. Found: C, 38.78; H, 5.77; N, 45.02.

Synthesis of (2-carbamimidamido-4-oxo-4,5-dihydro-1H-imidazol-5-yl)acetic acid 9. Yield 83%, mp 262–265°C; IR (potassium bromide): cm⁻¹ 3424–2808 (OH), 33801, 3210, 3175 (3NH, NH₂), 1667 (2C=O); ¹H-NMR: δ 10.17 (s, H, OH), 9.57 (s, 1H, NH), 8.33 (s, 2H, 2NH), 5.67 (br, 2H, NH₂), 5.17 (t, 1H, CH), 2.85 (d, 2H, CH₂); *Anal.* Calcd for C₆H₉N₅O₃ (199.17): C, 36.18; H, 4.55; N, 35.16. Found: C, 36.24; H, 4.59; N, 35.11.

Synthesis of 1-(5-sec-butyl-4-oxo-4,5-dihydro-1H-imidazol-2-yl)guanidine 10. Yield 87%, mp 285 (dec)°C; IR (potassium bromide): cm⁻¹ 3365, 3218, 3165 (3NH, NH₂), 1698 (C=O); ¹H-NMR: δ 9.12 (s, 1H, NH), 8.24 (s, 2H, 2NH), 5.61 (br, 2H, NH₂), 5.13 (d, 1H, CH), 2.23 (m, 1H, CH), 1.49 (m, 2H, CH₂), 1.10 (d, 3H, CH₃), 0.97 (t, 3H, CH₃); *Anal.* Calcd for C₈H₁₅N₅O (197.24): C, 48.72; H, 7.67; N, 35.51. Found: C, 48.85; H, 7.70; N, 35.44.

Synthesis of 1-[5-(1-hydroxyethyl)-4-oxo-4,5-dihydro-1H-imidazol-2-yl]guanidine 11. Yield 74%, mp 310 (dec)°C; IR (potassium bromide): cm⁻¹ 3403 (OH), 3366, 3238, 3167 (3NH, NH₂), 1674 (C=O); ¹H-NMR: δ 10.11 (s, 1H, OH), 9.32 (s, 1H, NH), 8.12 (s, 2H, 2NH), 5.61 (br, 2H, NH₂), 5.22 (d, 1H, CH), 4.86 (m, 1H, CH), 1.48 (d, 3H, CH₃); *Anal.* Calcd for C₆H₁₁N₅O₂ (185.18): C, 38.91; H, 5.99; N, 37.82. Found: C, 38.98; H, 6.03; N, 37.74.

Synthesis of 1-(5-isopropyl-4-oxo-4,5-dihydro-1H-imidazol-2-yl)guanidine 12. Yield 74%, mp 310 (dec)°C; IR (potassium bromide): cm⁻¹ 3388, 3216, 3164 (3NH, NH₂), 1687 (C=O); ¹H-NMR: δ 9.11 (s, 1H, NH), 8.23 (s, 2H, 2NH), 5.55 (br, 2H, NH₂), 5.03 (d, 1H, CH), 2.11 (m, 1H, CH), 1.04 (d, 6H, 2CH₃); *Anal.* Calcd for C₇H₁₃N₅O (183.21): C, 45.89; H, 7.15; N, 38.23. Found: C, 45.93; H, 7.17; N, 38.19.

Synthesis of 3-(2-carbamimidamido-4-oxo-4,5-dihydro-1H-imidazol-5-yl)propanoic acid 13. Yield 70%, mp 245 (dec)°C; IR (potassium bromide): cm⁻¹ 3419–2814 (2OH), 3385, 3219, 3171 (4NH, NH₂), 1664 (2C=O); ¹H-NMR: δ 10.23 (s, 2H, 2OH), 9.23 (s, 2H, NH), 8.24 (s, 2H, NH), 5.61 (br, 2H, NH₂), 5.36 (t, 1H, CH), 2.46 (t, 2H, CH₂), 2.12 (q, 2H, CH₂); *Anal.* Calcd for C₇H₁₁N₅O₃ (213.19): C, 39.44; H, 5.20; N, 32.85. Found: C, 39.51; H, 5.27; N, 32.79.

Synthesis of 1-[5-(hydroxymethyl)-4-oxo-4,5-dihydro-1H-imidazol-2-yl]guanidine 14. Yield 79%, mp 295 (dec)°C; IR (potassium bromide): cm⁻¹ 3401 (OH), 3341, 3210, 3155 (3NH, NH₂), 1687 (C=O); ¹H-NMR: δ 11.03 (s, 1H, OH), 9.22 (s, 1H, NH), 8.11 (s, 2H, 2NH), 5.60 (br, 2H, NH₂), 5.18 (t, 1H, CH), 4.17 (d, 2H, CH₂); *Anal.* Calcd for C₅H₉N₅O₂ (171.16): C, 35.09; H, 5.30; N, 40.92. Found: C, 35.14; H, 5.33; N, 40.86.

Synthesis of 2-(2-carbamimidamido-4-oxo-4,5-dihydro-1H-imidazol-5-yl)acetamide 15. Yield 88%, mp 263°C; IR (potassium bromide): cm⁻¹ 3323, 3202, 3105 (3NH, 2NH₂), 1691 (2C=O); ¹H-NMR: δ 9.25 (s, 1H, NH), 8.17 (s, 2H, NH), 5.66 (br, 2H, NH₂), 5.19 (t, 1H, CH), 4.10 (br, 2H, NH₂), 2.97 (d, 2H, CH₂); *Anal.* Calcd for C₆H₁₀N₆O₂ (198.18): C, 36.36; H, 5.09; N, 42.41. Found: C, 36.41; H, 5.11; N, 42.38.

Synthesis of 3-(2-carbamimidamido-4-oxo-4,5-dihydro-1H-imidazol-5-yl)propanamide 16. Yield 82%, mp >320°C; IR (potassium bromide): cm⁻¹ 3381, 3212, 3133 (3NH, 2NH₂), 1682 (2C=O); ¹H-NMR: δ 9.21 (s, 1H, NH), 8.04 (s, 2H, 2NH), 6.01 (br, 2H, NH₂), 5.11 (t, 1H, CH), 4.88 (br, 2H, NH₂), 2.49 (t, 2H, CH₂), 2.07 (m, 2H, CH₂); *Anal.* Calcd for C₇H₁₂N₆O₂ (212.21): C, 39.62; H, 5.70; N, 36.60. Found: C, 39.69; H, 5.74; N, 36.51.

Synthesis of 1-[3-(2-carbamimidamido-4-oxo-4,5-dihydro-1H-imidazol-5-yl)propyl]guanidine 17. Yield 68%, mp 270°C; IR (potassium bromide): cm⁻¹ 3381, 3226, 3141 (5NH, 2NH₂), 1662 (C=O); ¹H-NMR: δ 9.45 (s, 2H, 2NH), 8.37 (s, 3H, 3NH), 5.87 (br, 2H, NH₂), 5.29 (br, 2H, NH₂), 5.01 (t, 1H, CH), 3.38 (t, 2H, CH₂), 2.16 (q, 2H, CH₂), 1.88 (m, 2H, CH₂); *Anal.* Calcd for C₈H₁₆N₈O (240.26): C, 39.99; H, 6.71; N, 46.64. Found: C, 40.02; H, 6.74; N, 46.59.

Synthesis of 1-[5-(4-aminobutyl)-4-oxo-4,5-dihydro-1H-imidazol-2-yl]guanidine 18. Yield 78%, mp 225°C; IR (potassium bromide): cm⁻¹ 3388, 3223, 3171 (3NH, 2NH₂), 1661 (C=O); ¹H-NMR: δ 9.13 (s, 1H, NH), 8.16 (s, 2H, 2NH), 5.94 (br, 2H, NH₂), 5.30 (br, 2H, NH₂), 4.97 (t, 1H, CH), 3.23 (t, 2H, CH₂), 2.48 (q, 2H, CH₂), 1.81 (m, 2H, CH₂), 1.42 (m, 2H, CH₂); *Anal.* Calcd for C₈H₁₆N₆O (212.25): C, 45.27; H, 7.60; N, 39.59. Found: C, 45.30; H, 7.63; N, 39.50.

Synthesis of 1-[3-(2-carbamimidamido-4-oxo-4,5-dihydro-1H-imidazol-5-yl)propyl]urea 19. Yield 74%, mp 325°C; IR (potassium bromide): cm⁻¹ 3383, 3220, 3177 (4NH, 2NH₂), 1666 (2C=O); ¹H-NMR: δ 9.19 (s, 1H, NH), 8.10 (s, 2H, 2NH), 6.38 (s, 1H, NH), 5.89 (br, 2H, NH₂), 5.58 (br, 2H, NH₂), 4.94 (t, 1H, CH), 3.13 (t, 2H, CH₂), 2.19 (q, 2H, CH₂), 1.55 (m, 2H, CH₂); *Anal.* Calcd for C₈H₁₅N₇O₂ (241.25): C, 39.83; H, 6.27; N, 40.64. Found: C, 39.88; H, 6.30; N, 40.59.

Synthesis of N-carbamoylimidodicarbonimidic diamide 20. Yield 83%, mp 230°C; IR (potassium bromide): cm⁻¹ 3379, 3262, 3186 (4NH, NH₂), 1674 (C=O); ¹H-NMR: δ 9.10 (s, 2H, 2NH), 8.02 (s, 2H, 2NH), 6.32 (br, 2H, NH₂), 3.75 (br, 2H, NH₂); *Anal.* Calcd for C₃H₈N₆O (144.13): C, 25.00; H, 5.59; N, 58.31. Found: C, 25.11; H, 5.67; N, 58.23.

Synthesis of N-(carbamimidoylcarbamimidoyl)acetamide 21. Yield 79%, mp 250 (dec)°C; IR (potassium bromide): cm⁻¹ 3381, 3260, 3188 (4NH, 2NH₂), 1677 (C=O); ¹H-NMR: δ 10.07 (s, 1H, NH), 7.65 (s, 3H, 3NH), 6.85 (br, 2H, NH₂), 2.08 (s, 3H, CH₃); *Anal.* Calcd for C₄H₉N₅O (143.15): C, 33.56; H, 6.34; N, 48.92. Found: C, 33.63; H, 6.41; N, 48.81.

Synthesis of N-(carbamimidoylcarbamimidoyl)benzamide 22. Yield 75%, mp 145°C; IR (potassium bromide): cm⁻¹ 3371, 3215, 3173, 3104 (4NH, NH₂); ¹H-NMR: δ 11.47 (s, 1H, NH), 8.12 (s, 3H, 3NH), 7.69–7.25 (m, 5H, arom), 6.22 (br, 2H, NH₂); *Anal.* Calcd for C₉H₁₁N₅O (205.22): C, 52.68; H, 5.40; N, 34.13. Found: C, 52.74; H, 5.49; N, 34.04.

Synthesis of N-[(2,5-dioximidazolidin-4-yl)carbamoyl]imidodicarbonimidic diamide 23. Yield 81%, mp 270°C; IR (potassium bromide): cm⁻¹ 3382, 3265, 3189, 3112 (7NH, NH₂); ¹H-NMR: δ 11.67 (s, 1H, NH), 9.43 (s, 1H, NH), 9.27 (s, 1H, NH), 9.14 (s, 1H, NH), 8.14 (s, 3H, 3NH), 6.32 (s, 1H, CH), 5.48 (br, 2H, NH₂); *Anal.* Calcd for C₆H₁₀N₈O₃ (242.20): C, 29.76; H, 4.16; N, 46.27. Found: C, 29.81; H, 4.20; N, 46.18.

Synthesis of 4-(carbamimidoylcarbamimidamido)benzoic acid 24. Yield 72%, mp 280 (dec)°C; IR (potassium bromide): cm⁻¹ 3416–2840 (OH), 3388, 3140 (4NH, NH₂), 1685 (C=O); ¹H-NMR: δ 10.55 (s, 1H, OH), 9.47 (s, 2H, 2NH), 8.23 (s, 2H, 2NH), 7.53–6.43 (br, 4H, arom), 4.47 (br, 2H, NH₂); *Anal.*

Calcd for $C_9H_{12}N_5O_2$ (222.22): C, 48.64; H, 5.44; N, 31.51. Found: C, 48.72; H, 5.51; N, 31.42.

Synthesis of 4-(carbamimidoylcarbamimidamido)benzenesulfonic acid 25. Yield 72%, mp $>320^\circ\text{C}$; IR (potassium bromide): cm^{-1} 3477 (OH), 3395, 3162 (4NH, NH_2); $^1\text{H-NMR}$: δ 10.34 (s, 1H, OH), 9.24 (s, 2H, NH), 8.07 (s, 2H, 2NH), 7.57–7.12 (br, 4H, arom), 5.14 (br, 2H, NH_2); *Anal.* Calcd for $C_8H_{11}N_5O_3S$ (257.27): C, 37.35; H, 4.31; N, 27.22; S, 12.46. Found: C, 37.44; H, 4.39; N, 27.11; S, 12.20.

Synthesis of N-9H-purin-6-ylimidodicarbonimidic diamide 26. Yield 69%, mp 350°C ; IR (potassium bromide): cm^{-1} 3408, 3388, 3140 (5NH, NH_2); $^1\text{H-NMR}$: δ 10.07 (s, 1H, NH), 9.22 (s, 2H, 2NH), 8.12 (s, 2H, 2NH), 7.88 (s, 1H, CH), 6.74 (s, 1H, CH), 5.04 (br, 2H, NH_2); *Anal.* Calcd for $C_7H_9N_9$ (219.21): C, 38.35; H, 4.14; N, 57.51. Found: C, 38.47; H, 4.19; N, 57.44.

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