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EFFICIENT SYNTHESIS OF PYRIMIDINECARBONITRILES AND THEIR DERIVATIVES

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Abstract – New approach to pyrimidinecarbonitriles was developed. Pyrimidine-4- and 6-carbonitriles were prepared by palladium-catalyzed cross-coupling reaction of iodopyrimidines with $\text{Zn}(\text{CN})_2$ in very good yields. The cyano group was converted into the corresponding acyl groups by the treatment with Grignard reagents and transformed to amido and imido function as well.

INTRODUCTION

Pyrimidine derivatives bearing carbon substituents may lead to the potential biologically active nucleoside analogues e.g. cytostatics,¹ antivirals,² adenosine receptor antagonists,³ cyclin dependent kinase inhibitors,⁴ antibacterial agents⁵ or adenosine kinase inhibitors.⁶

Pyrimidinecarbonitriles are versatile intermediates for the synthesis of many C-substituted pyrimidine derivatives. Preparative methods of the pyrimidinecarbonitriles reported in the literature are nucleophilic substitution of halopyrimidine derivatives with cyanide ion⁷ or reaction of pyrimidine N-oxides with cyanide ion in the presence of acylating reagent (Reissert-Henze reaction).⁸ The first described method involves cyanation of chloropyrimidines using NaCN in DMSO and affords pyrimidinecarbonitriles in the yields about 30%. Pyrimidine N-oxides react with trimethylsilyl cyanide in the presence of base in moderate to good yields depending upon the substitution of the pyrimidine ring to afford pyrimidine-2- and 6-carbonitriles. 2-Amino-4-methylpyrimidine-6-carbonitrile and 2-aminopyrimidine-4,6-dicarbonitrile were prepared by nitrosation of 2-amino-4,6-dimethylpyrimidine followed by dehydration of iminoxy derivative by POCl_3 in the yields about 25%.⁹

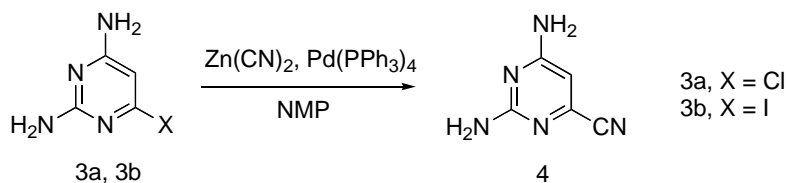
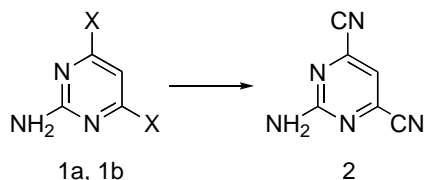
It is known from literature that the cross-coupling reaction of aryl halides with KCN in the presence of a palladium complex was effective for preparation of aryl cyanides.¹⁰ Cross-coupling reaction employing KCN and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in DMF¹¹ or $\text{Zn}(\text{CN})_2$ and $\text{Pd}(\text{PPh}_3)_4$ in NMP¹² was also described for preparation of purinecarbonitriles.

RESULTS AND DISCUSSION

In this paper, we report on the synthesis of 2-aminopyrimidine-4,6-dicarbonitrile (**2**) and 2,4-diaminopyrimidine-6-carbonitrile (**4**) by means of the palladium catalyzed cross-coupling reaction of iodopyrimidines with $\text{Zn}(\text{CN})_2$. We were interested in introduction of cyano function onto the pyrimidine ring to obtain analogues of alkynylpyrimidine derivatives that possess cytostatic activity.¹ The dichloropyrimidine **1a** was unreactive towards copper(I) cyanide in DMF at 150 °C while reaction of dichloropyrimidine **1a** with $\text{Zn}(\text{CN})_2$ in NMP catalyzed by $\text{Pd}(\text{PPh}_3)_4$ gave desired dicarbonitrile **2** in a low yield. This problem was solved by conversion of dichloropyrimidine **1a** to 2-amino-4,6-diiodopyrimidine (**1b**) by procedure using hydroiodic acid (57%) and sodium iodide.^{1,6} The diiodopyrimidine **1b** reacted smoothly with $\text{Zn}(\text{CN})_2$ in NMP under catalysis by $\text{Pd}(\text{PPh}_3)_4$. NMP is a solvent of choice since the reaction in DMF affords product **2** in a low yield. Reactions catalyzed by $\text{PdCl}_2(\text{PPh}_3)_2$ failed (Scheme 1, Table 1). Also 2,4-diaminopyrimidine-6-carbonitrile (**4**) was prepared from 2,4-diamino-6-iodopyrimidine (**3b**) by the same procedure as dicarbonitrile **2** in 84% yield. Commercially available 2,4-diamino-6-chloropyrimidine (**3a**) was converted to iodo derivative **3b** by treatment with 57% hydroiodic acid and NaI.

Table 1: Synthesis of 2-aminopyrimidine-4,6-dicarbonitrile **2**

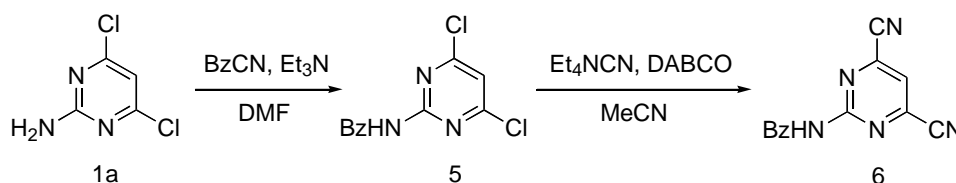
Compd	X	Conditions	Yield of 2 (%)
1a	Cl	CuCN, DMF	n.r.
1a	Cl	$\text{Zn}(\text{CN})_2$, $\text{Pd}(\text{PPh}_3)_4$, NMP	7
1a	Cl	KCN, $\text{PdCl}_2(\text{PPh}_3)_4$, DMF	n.r.
1b	I	$\text{Zn}(\text{CN})_2$, $\text{Pd}(\text{PPh}_3)_4$, NMP	88
1b	I	$\text{Zn}(\text{CN})_2$, $\text{Pd}(\text{PPh}_3)_4$, DMF	26
1b	I	$\text{Zn}(\text{CN})_2$, $\text{PdCl}_2(\text{PPh}_3)_4$, DMF	n.r.
1b	I	KCN, $\text{PdCl}_2(\text{PPh}_3)_4$, DMF	n.r.



Scheme 1

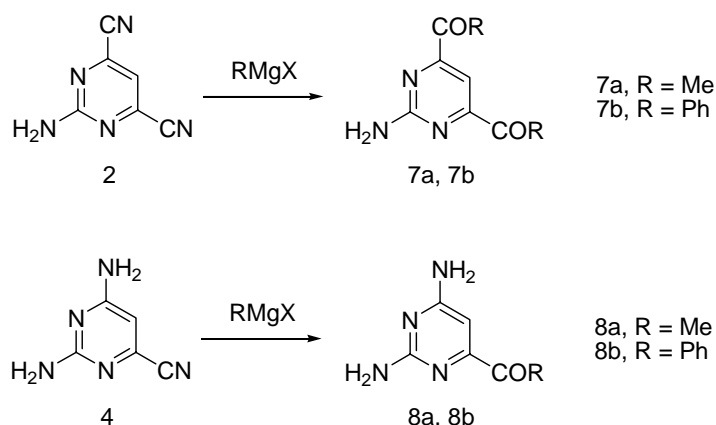
We also tried to prepare pyrimidinecarbonitrile derivatives by treatment of halopyrimidine with tetraethylammonium cyanide (TEACN) in the presence of base. This method was reported for the synthesis of purine-6-carbonitrile derivatives.¹³ The amino group was protected by benzoylation. Reaction of 2-amino-4,6-dichloropyrimidine (**1a**) with benzoyl chloride gave protected pyrimidine in a low yield^{3,14} and that's why we used benzoyl cyanide in the presence of triethylamine.¹⁵ Because of the poor solubility of

starting material the best yields were obtained using DMF as a solvent. Reaction of protected pyrimidine **5** with TEACN in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) afforded desired carbonitrile **6** in a low yield (8%). This can be explained by formation of a stable quaternary ammonium salt of DABCO with pyrimidine. This ammonium salt does not further react with TEACN (Scheme 2).



Scheme 2

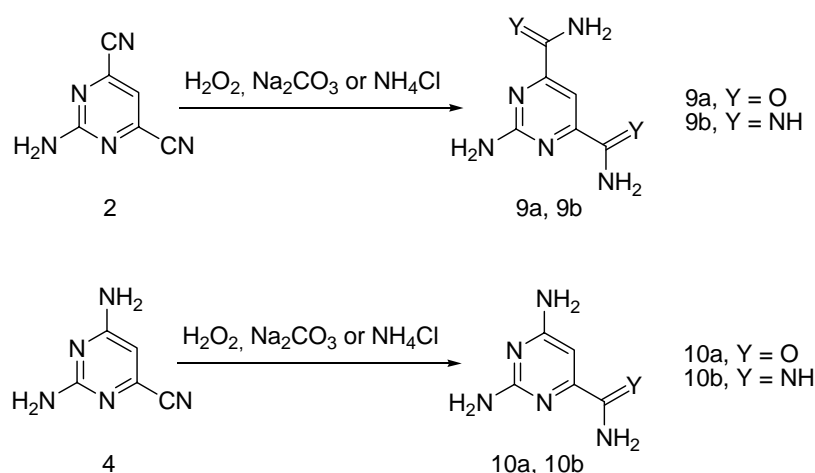
We have further investigated the conversion of the cyano group into the acyl group by treatment with Grignard reagent e.g. phenylmagnesium chloride or methylmagnesium iodide.^{11,16} Treatment of **2** with methylmagnesium iodide and phenylmagnesium chloride in THF at room temperature gave corresponding carbonyl derivatives **7a** and **7b** by the addition of the Grignard reagents to the CN triple bond, selectively. Reactions with allylmagnesium bromide or benzylmagnesium chloride afforded complex mixtures of products. Although the reaction of **4** with phenylmagnesium chloride afforded desired product **8b** in 32% yield, the reaction of **4** with methylmagnesium iodide afforded inseparable mixture of the starting material with product **8a** (1:3) (Scheme 3).



Scheme 3

Pyrimidinecarbonitriles **2** and **4** were also treated with hydrogen peroxide in an aqueous Na_2CO_3 ¹⁷ to afford corresponding carboxamide derivatives **9a** and **10a** in good yields. On treatment with a catalytic amount of sodium methoxide in methanol compounds **2** and **4** formed imidate intermediates that were without

isolation treated with ammonium chloride to afford amidines **9b** and **10b** which were isolated by preparative HPLC using gradient of TEAB (Scheme 4).



Scheme 4

Our attempts to reduce cyano function to formyl or aminomethyl group failed. The hydrogenation of the compound **2** in methanol over palladium on charcoal in acidic conditions¹⁸ afforded 2-aminopyrimidine-4-carbonitrile (**11**) in a yield of 23%. The reduction using DIBAL in THF¹⁹ did not proceed at all and the starting material was recovered.

Compounds **2**, **4** and **7a**, **7b**, **8b**, **9a**, **9b**, **10a**, **10b** and **11** were tested for their cytostatic and/or antiviral activity. None of these compounds exhibited any significant cytostatic or cytotoxic activity.

In conclusion, we developed an efficient synthesis of pyrimidine carbonitriles by Pd mediated cross-coupling reaction with $\text{Zn}(\text{CN})_2$. 2-Aminopyrimidine-4,6-dicarbonitrile and 2,4-diaminopyrimidine-6-carbonitrile were further transformed to acyl, amide and amidine derivatives. None of these compounds possess significant cytostatic and/or antiviral activity.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Unless otherwise stated, solvents were evaporated at 40 °C/2 kPa and compounds were dried overnight at 2 kPa over P₂O₅. Melting points were determined on a Büchi Melting Point B-545 apparatus and are uncorrected. TLC was performed on plates of Kieselgel 60 F254 (Merck). NMR spectra were measured on an FT NMR spectrometer Varian UNITY 500 (¹H at 500 MHz and ¹³C at 125.7 MHz) in dimethyl sulfoxide-*d*₆. Chemical shifts (δ ppm) and coupling constants (*J*, Hz) were obtained by the first-order analysis of the spectra. Mass spectra were measured on a ZAB-EQ (VG Analytical) spectrometer using FAB (ionization by Xe, accelerating voltage 8 kV, glycerol matrix).

Preparative HPLC purification was performed on a column packed with 10 μm C18 reversed phase (Luna), 250 x 21 mm; in ca 300 mg portions of mixtures using linear gradient H₂O – MeOH (20 – 100% of MeOH in 60 min) or in 0.1 M triethylammonium hydrogen carbonate (TEAB) in water and in 50% MeOH (linear gradient of TEAB in 50% MeOH, 0 – 100%).

2-Amino-4,6-diiodopyrimidine (1b): 2-Amino-4,6-dichloropyrimidine (3 g, 18 mmol), NaI (13.5 g, 89 mmol) and 57% HI (17 mL) in acetone (90 mL) was stirred overnight at rt. The precipitate was filtered, washed with ice cold water and acetone, yield 4.65 g (73%), mp 222 – 224 °C (decomp). MS (FAB) *m/z*: 347.8 [MH⁺] (100). ¹H NMR (DMSO-*d*₆): 7.45 (s, 1H, H-5); 7.35 (br s, 2H, NH₂). ¹³C NMR (DMSO-*d*₆): 161.62 (C-2); 130.71 (2C, C-4 and C-6); 128.52 (C-5).

General procedure for cross-coupling of dihalopyrimidines (1a or 1b) with Zn(CN)₂: A mixture of a dihalopyrimidine (1mmol), Zn(CN)₂ (1.2 mmol) and the catalyst (see Table 1) (0.1 mmol) in NMP or DMF (6 mL) was heated at 100 °C under Ar atmosphere for 4 - 16 h. The reaction mixture was cooled and 2M aq. ammonia was added. The mixture was extracted with EtOAc (3 x 50 mL), the combined organic extracts were washed with brine (1 x 50 mL), dried with MgSO₄ and evaporated. The crude product was purified by flash chromatography in a gradient of MeOH (0 – 5%) in CHCl₃ and crystallized from water.

2-Amino-4,6-dicarbonitrile (2): White crystalline product, yield 88%, mp 201 °C (decomp). MS (EI) *m/z*: 145.2 [M⁺] (100). HRMS (EI): found 145.0386, calculated for C₆H₃N₅: 145.0388. ¹H NMR (DMSO-*d*₆): 7.94 (br s, 2H, NH₂); 7.72 (s, 1H, H-5). ¹³C NMR (DMSO-*d*₆): 163.50 (C-2); 143.55 (2C, C-4 and C-6); 115.38 (2C, CN); 115.27 (C-5). *Anal.* Calcd for C₆H₃N₅: C, 49.66; H, 2.08; N, 48.26. Found.: C, 49.41; H, 2.04; N, 48.11.

2,4-Diamino-6-iodopyrimidine (3b): To the suspension of 2,4-diamino-6-chloropyrimidine (5 g, 35 mmol) and NaI (15 g, 99 mmol) in 57% HI (50 mL) acetone (20 mL) was added and the resulting mixture was heated at 50 °C for 30 min and then stirred at rt overnight. The precipitate was collected by suction, taken to ethyl acetate and washed with aqueous NaHCO₃ and brine and dried with MgSO₄. The crude product was used without further purification, yield 6.7 g (82%), mp 188 °C. MS (EI) *m/z*: 236 [M⁺] (76).

^1H NMR (DMSO- d_6): 6.42 (br s, 2H) and 6.25 (br s, 2H, NH₂); 6.13 (s, 1H, H-5). ^{13}C NMR (DMSO- d_6): 163.54 (C-4); 162.08 (C-2); 128.20 (C-6); 104.09 (C-5).

2,4-Diaminopyrimidine-6-carbonitrile (4): A mixture of 2,4-diamino-6-iodopyrimidine **3b** (1 g, 4.2 mmol), Zn(CN)₂ (300 mg, 2.5 mmol) and Pd(PPh₃)₄ (529 mg, 0.42 mmol) in NMP (20 mL) was heated at 100°C under Ar atmosphere for 2 h. The reaction mixture was cooled and 2M aq. ammonia was added. The mixture was extracted with EtOAc (3 x 100 mL), the combined organic extracts were washed with brine (1 x 100 mL), dried with MgSO₄ and evaporated. The crude product was purified by flash chromatography in a gradient of MeOH (0 – 10%) in CHCl₃, crystallization from EtOH afforded 2,4-diaminopyrimidine-6-carbonitrile **4** as white crystals (0.48g, 84%), mp 244 °C (decomp). MS (EI) m/z: 135 [M⁺] (100). ^1H NMR (DMSO- d_6): 6.91 (br s, 2H) and 6.46 (br s, 2H, NH₂); 6.13 (s, 1H, H-5). ^{13}C NMR (DMSO- d_6): 164.36 (C-4); 163.80 (C-2); 138.93 (C-6); 117.42 (CN); 99.95 (C-5). *Anal.* Calcd for C₅H₅N₅: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.23; H, 3.53; N, 51.88.

N-(4,6-Dichloropyrimidin-2-yl)benzamide (5): 2-Amino-4,6-dichloropyrimidine **1a** (4 g, 24.4 mmol), benzoyl cyanide (3.6 mL, 30 mmol) and Et₃N (1 mL) in DMF (60 mL) was stirred under Ar atmosphere for 72 h. The reaction mixture was evaporated *in vacuo* and crystallization from EtOAc – light petroleum mixture afforded white crystalline product (4.7 g, 72%), mp 186 °C. MS (FAB) m/z: 268 [MH⁺] (100). HRMS (FAB): found 268.0035, calculated for C₁₁H₈N₃OCl₂: 268.0044. ^1H NMR (DMSO- d_6): 11.56 (br s, 1H, NH); 7.96 (d, 2H), 7.62 (t, 1H) and 7.52 (t, 2H, arom.); 7.69 (s, 1H, H-5). ^{13}C NMR (DMSO- d_6): 165.51 (C=O); 161.50 (2C, C-4 and C-6); 157.94 (C-2); 133.61, 128.78 (2C), 128.43 (2C) and 127.94 (arom.); 116.32 (C-5).

N-(4,6-Dicyanopyrimidin-2-yl)benzamide (6): To stirred solution of the protected dichloropyrimidine **5** (1.08 g, 4 mmol) and TEACN (2.48 g, 16 mmol) in dry acetonitrile (80 mL) at -20°C DABCO (1.8 g, 16 mmol) was added and the resulting solution was allowed to stand overnight at rt. The solvent was evaporated (the reaction mixture turned dark brown during evaporation) and the residue was purified by column chromatography in CHCl₃, the crude product was crystallized from EtOAc – light petroleum mixture to give protected 4,6-dicyanopyrimidine **6** (83 mg, 8%) as yellow crystals, mp 174 °C (decomp). MS (EI) m/z: 249 [M⁺] (79). ^1H NMR (DMSO- d_6): 11.88 (br s, 1H, NH); 8.5 (s, 1H, H-5); 7.98 (m, 1H) and 7.61 (m, 4H, arom.). ^{13}C NMR (DMSO- d_6): 165.66 (C=O); 159.08 (C-2); 158.33 (C-4); 143.60 (C-6); 133.41, 133.08 and 128.75 (arom.); 123.12 (C-5); 115.10 (CN).

General procedure for reaction with Grignard reagents: To the solution of pyrimidinedicarbonitrile **2** (1 mmol) or pyrimidinecarbonitrile **4** (1 mmol) in dry THF (10 mL) was added dropwise solution of phenylmagnesium chloride (2M solution in THF, 4 mmol) or methylmagnesium iodide (solution in Et₂O, 4 mmol), the reaction mixture was stirred under Ar atmosphere at rt overnight; 15 mL of water and 15 mL of 3M HCl was added and the reaction mixture was extracted with ethyl acetate (3 x 50 mL), combined

organic extracts were washed with brine (2 x 50 mL) and dried with MgSO₄. The crude product was purified by flash chromatography in a gradient of MeOH in CHCl₃.

1,1'-(2-Aminopyrimidine-4,6-diyl)diethanone (7a): Crystallized from water, yellow crystals, yield 17%, mp 146 °C. MS (EI) m/z: 179.1 [M⁺] (100). ¹H NMR (DMSO-*d*₆): 7.36 (br s, 1H) and 7.27 (br s, 1H, NH₂); 2.55 (s, 6H, CH₃). ¹³C NMR (DMSO-*d*₆): 199.49 (2C, C=O); 164.46 (C-2); 162.26, (2C, C-4 and C-6); 100.82 (C-5); 25.67 (2C, CH₃). *Anal.* Calcd for C₆H₇N₅O₂: C, 53.63; H, 5.06; N, 23.45; O, 17.86. Found: C, 53.44; H, 5.26; N, 23.59.

(2-Aminopyrimidine-4,6-diyl)bis(phenylmethanone) (7b): Crystallized from EtOH, white crystals, yield 43%, mp 185 °C. MS (FAB) m/z: 304.2 [MH⁺] (100). ¹H NMR (DMSO-*d*₆): 7.39 (br s, 2H, NH₂); 7.22 (s, 1H, H-5); 8.00 (d, 4H), 7.72 (t, 2H), 7.58 (t, 4H) (arom). ¹³C NMR (DMSO-*d*₆): 193.00 (2C, C=O); 164.80 (2C, C-4 and C-6); 162.64 (C-2); 134.91 (2C), 134.12 (2C), 130.66 (4C) and 128.80 (4C, arom); 106.08 (C-5). *Anal.* Calcd for C₁₈H₁₃N₃O₂: C, 71.28; H, 4.32; N, 13.85; O, 10.55. Found: C, 71.16; H, 4.35; N, 13.59.

1-(2,4-Diaminopyrimidin-6-yl)ethanone (8a): To the reaction mixture was added additional methylmagnesium iodide (4 mmol) and the reaction mixture was heated at 45 °C for 8 h. Purified by preparative HPLC using linear gradient of MeOH, isolated as an inseparable mixture of product with starting material (3:1, 105 mg). MS (FAB) m/z: 153.1 [MH⁺] (100). ¹H NMR (DMSO-*d*₆): 6.75 and 6.28 (2 x br s, 2 x 2H, NH₂); 6.23 (s, 1H, H-5); 2.43 (s, 1H, CH₃).

(2,4-Diaminopyrimidin-6-yl)(phenyl)methanone (8b): Crystallized from EtOH – Et₂O mixture, yellow crystals, yield 32%, mp 177 °C (decomp). MS (FAB) m/z: 215 [MH⁺] (100). HRMS (FAB): found 215.0927, calculated for C₁₁H₁₀N₄O: 215.0932. ¹H NMR (DMSO-*d*₆): 7.93 (d, 2H), 7.64 (7, 1H) and 7.52 (t, 2H, arom); 6.65 (br s, 2H) and 6.19 (br s, 2H, NH₂); 6.06 (s, 1H, H-5). ¹³C NMR (DMSO-*d*₆): 194.43 (C=O); 165.18 (C-4); 163.21 (C-2); 161.75 (C-6); 135.92, 133.40, 130.35 (2C) and 128.53 (2C, arom); 94.28 (C-5).

2-Aminopyrimidine-4,6-dicarboxamide (9a): Acetone (5 mL) was added to a mixture of **2** (200 mg, 1.38 mmol) in 10% aqueous Na₂CO₃ until uniform solution was obtained, 10% H₂O₂ (5 mL) was added dropwise and the resulting mixture was allowed to stir at rt for 6 h. The reaction mixture was evaporated *in vacuo*, the crude product was crystallized from H₂O – EtOH mixture to give white crystalline product (191 mg, 77%), mp 320 °C (decomp). MS (EI) m/z: 181.1 [M⁺] (100). ¹H NMR (DMSO-*d*₆): 7.84 (br s, 2H), 7.80 (br s, 2H), 7.05 (br s, 2H) (NH₂); 7.53 (s, 1H, H-5). ¹³C NMR (DMSO-*d*₆): 165.23 (2C, C=O); 163.07 (C-2); 160.74 (2C, C-4 and C-6); 103.66 (C-5). *Anal.* Calcd for C₆H₇N₅O₂: C, 39.78; H, 3.89; N, 38.66; O, 17.66. Found: C, 39.61; H, 3.78; N, 38.56.

2-Aminopyrimidine-4,6-dicarboxamidine (9b): To the solution of **2** (200 mg, 1.38 mmol) in MeOH (160 mL) was added 1M solution of MeONa in MeOH (0.276 mL, 0.276 mmol) and the resulting mixture was stirred for 2 days at rt. Then NH₄Cl (300 mg, 5.52 mmol) was added and the reaction mixture was

refluxed for 3h and evaporated *in vacuo*. The crude product was purified by preparative HPLC using gradient of TEAB. Yellowish powder (55 mg, 22%), mp 305 – 308 °C (decomp). MS (EI) m/z: 179 [M⁺] (15). HRMS (EI): found 179.0911, calculated for C₆H₉N₇: 179.0919. ¹H NMR (DMSO-*d*₆): 7.86 (br s, 2H), 7.80 (br s, 2H), 7.78 (br s, 2H) and 7.05 (br s, 2H, NH); 7.53 (s, 1H, H-5). ¹³C NMR (DMSO-*d*₆): 165.21 (2C, C-4, C-6); 163.05 (C-2); 160.75 (2C, CN); 103.64 (C-5).

2,4-Diaminopyrimidine-6-carboxamide (10a): Prepared according the procedure described for compound **9a**. Crystallized from water, white crystals (124 mg, 55%), mp 284 °C (decomp). MS (EI) m/z: 153.1 [M⁺] (35). HRMS (EI): found 153.0647, calculated for C₅H₇N₅O: 153.0650. ¹H NMR (DMSO-*d*₆): 7.54 (br s, 1H), 7.52 (br s, 1H), 6.61 (br s, 2H) and 6.33 (s, 2H, NH₂); 6.33 (s, 1H, H-5). ¹³C NMR (DMSO-*d*₆): 166.30 (C=O); 165.70 (C-4); 163.19 (C-2); 156.72 (C-6); 93.06 (C-5). *Anal.* Calcd for C₅H₇N₅O: C, 39.21; H, 4.61; N, 45.73; O, 10.45. Found: C, 38.98; H, 4.41; N, 45.74.

2,4-Diaminopyrimidine-6-carboximidine (10b): Prepared according to the procedure described for compound **9b**. Crystallized from hot water, white crystals (130 mg, 58%), mp 210 °C (decomp). MS (ESI) m/z: 153 [MH⁺] (100). ¹H NMR (DMSO-*d*₆): 8.00 (br s, 5H), 6.93 (br s, 1H) and 6.29 (br s, 1H, NH); 6.315 (s, 1H, H-5). ¹³C NMR (DMSO-*d*₆): 165.20 (C-4); 163.66 and 163.43 (C-2 and C=N); 152.00 (C-6); 94.55 (C-5). *Anal.* Calcd for C₅H₈N₆: C, 39.47; H, 5.30; N, 55.23. Found: C, 39.41; H, 5.40; N, 55.05.

2-Aminopyrimidine-4-carbonitrile (11): 2-Aminopyrimidine-4,6-dicarbonitrile (**2**, 400 mg, 1.38 mmol) was hydrogenated in MeOH (40 mL) and hydrochloric acid (0.2 mL) over 5% palladium on charcoal (0.16 g) under stirring for 18 h at rt. The mixture was filtered through a pad of Celite and the catalyst was washed with MeOH. The filtrate was neutralized with methanolic ammonia and evaporated (during evaporation the reaction mixture turned violet). The crude product was purified by column chromatography on silica gel (elution with 0 – 3% MeOH in CHCl₃) to give 98 mg (23%) of 2-aminopyrimidine-4-carbonitrile **11**, mp 222 °C (decomp). MS (EI) m/z: 120.0 [M⁺] (100). ¹H NMR (DMSO-*d*₆): 8.51 (br s, 1H, H-6); 7.07 (br s, 1H, H-5); 7.32 (br s, 2H, NH₂). ¹³C NMR (DMSO-*d*₆): 163.71 (C-2); 161.19 (C-6); 140.88 (C-4); 116.49 (CN); 112.97 (C-5). *Anal.* Calcd for C₅H₄N₄: C, 50.00; H, 3.36; N, 46.65. Found: C, 49.89; H, 3.28; N, 46.55.

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