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*N*-[(5-Cyano-2-oxoimidazolidin-4-yl)-iminomethyl]-*p*-toluenesulfonamide **3** was prepared in fairly good yield by the base catalyzed cyclisation of *N*-[(*Z*)-2-amino-1,2-dicyanovinylcarbamoyl]-*p*-toluenesulfonamide **2**. The *N*-[(*Z*)-2-amino-1,2-dicyanovinyl carbamoyl]-*p*-toluenesulfonamide **2** was reacted readily with two molar amount of *p*-nitrobenzaldehyde at room temperature in the presence of base to give 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide **8**. Thiation of compounds **3** and **8** using Lawesson's reagent in tetrahydrofuran gave novel thioimidazoles **4**, **5**, and **6** and thiopurines **9**, **10**, and **11**, which have been characterized spectroscopically.

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## Introduction.

In the last decade diaminomaleonitrile **1** (DAMN) has received much interest as a source of nitrogen heterocycles. The reactions most widely used in those syntheses are condensations with carbonyl compounds. One approach is exemplified by the photochemical conversion of DAMN **1** into 4-amino-5-cyanoimidazole [1] resulting from the *trans* isomer, diaminofumaronitrile [2]. No chemical reactions of *trans* isomer, however, are known mainly because it reverts to the *cis* isomer **1** under the influence of acid, base, charcoal, light or heating [3]. Again many of the chemical properties of these imidazoles are still unknown. In this investigation DAMN **1** is used as *cis*-1,2-diaminoethylene component.

We would like to report here a reaction pattern of DAMN **1**, in which **1** is used as a *cis* 1,2-diaminoethylene component. This is demonstrated by the successive reaction of **1** with isocyanate to give imidazole, this result is inconsistent to the result described by Ohtsuka *et al.* [4] in the base catalyzed cyclisation of *N*-[(*Z*)-2-amino-1,2-dicyanovinylcarbamoyl]-*p*-toluenesulfonamide **2**.

We have been particularly interested in developing a route to the hitherto unknown compound **2** as a precursor in the synthesis of a range of new 1,2-dihydropurine and purine derivatives. We now report the successful synthesis of compound **2** as a precursor for the preparation of new 1,2-dihydropurines **7** and 6-carbamoyl-purines **8**.

It was reported that the angular 7*H*-1,2,3-triazolo[3,4-*i*]purine analogues have been investigated recently for their potential xanthine oxidase inhibitory activities [5]. Allopurinol is known to inhibit xanthine oxidase [6] and is now widely employed in the treatment of gout and hyperuricemia resulting from uric acid [6-8]. No clinically effective xanthine oxidase inhibitors for the treatment of hyperuricemia have been developed since allopurinol was introduced for clinical use in 1963 [6]. In addition, purine analogues are useful as anticancer and antiviral agent [9].

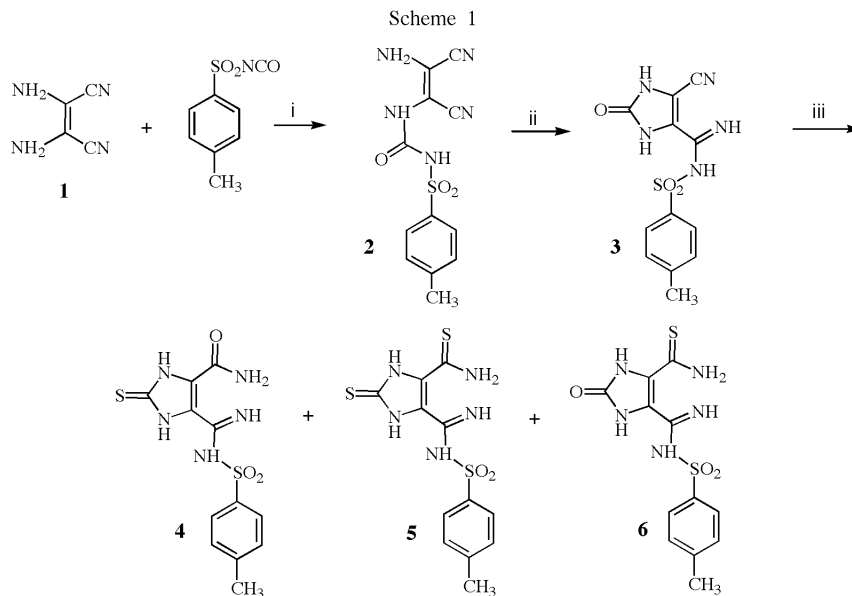
Recently, we are concerned with the thiohydantoin derivatives [10] used as potential hypolipidemic agents [11], bearing imidazole-2-thione functional group and responsible for biological activity. The reported biological importance of thione compounds prompted us to try the conversion of *N*-[(5-cyano-2-oxoimidazolidin-4-yl)-iminomethyl]-*p*-toluenesulfonamide **3** and 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide **8** into the corresponding thione derivatives **4-6** and **9-11** respectively, to search for active and less toxic compounds.

## Results and Discussion.

When DAMN **1** was allowed to react with tosylisocyanate, compound **2** was produced. Cyclisation reaction of compound **2** with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene in acetonitrile produced compound **3** in fairly high yield (93%). This result is inconsistent to that obtained by Ohtsuka *et al.* for cyclisation of compound **2** to the cytosine derivatives under the same reaction conditions [4].

The infrared spectra of compound **2** showed a strong stretching vibration at 1645 cm<sup>-1</sup> due to the carboxamide ν C=O. The characteristic feature of compound **2** is a strong C≡N stretching vibration at 2209 cm<sup>-1</sup> and a weak cyano stretching vibration at 2255 cm<sup>-1</sup> as shown in Table 1. The <sup>1</sup>H NMR spectrum of compound **2** exhibit a broad singlet signal for the acidic proton at δ 11.17 of (-CO-NHSO<sub>2</sub>Ar), singlet signals at δ 7.77 for the (-CO-NH-C-) and a broad singlet signal having a shoulder at δ 7.38 ppm for the (-C=CCNNH<sub>2</sub>) as illustrated in Table 1.

The infrared spectra of compound **3** showed the appearance of a strong stretching vibration at 1724 cm<sup>-1</sup> for ν C=O in the imidazol-2-one ring characteristic of the five membered ring and a weak C≡N stretching vibration at 2231 cm<sup>-1</sup> as shown in Table 1. The <sup>1</sup>H NMR spectrum of compound **3** exhibit a broad singlet signal at δ 11.51 for two proton of (-NH-) and the two singlet signals having a shoulder at δ 8.41-8.37 for two protons of (-NH) groups in the imidazol-2-one ring.

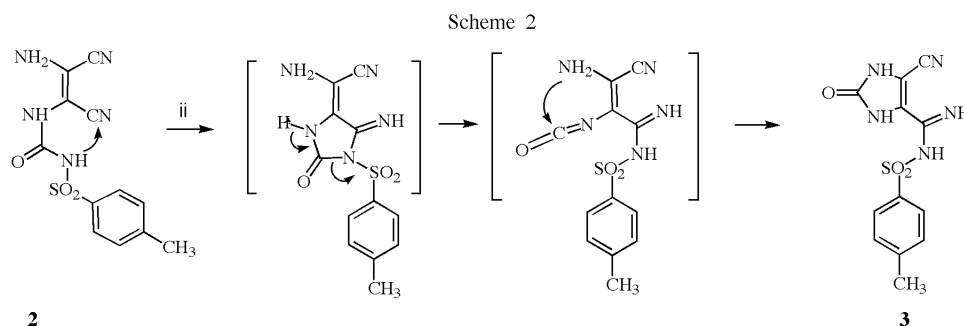


Reagents and conditions; i) Acetonitrile/under nitrogen at 0 °C for 15 minutes and then at room temperature for 10 minutes; ii) Acetonitrile/under nitrogen atmosphere at 0 °C then 5 mole % of 1,8-diazabicyclo[5.4.0]undec-7-ene/stirred at room temperature for 2 hours; iii) Lawesson reagent /tetrahydrofuran refluxing under nitrogen for 12 hours.

A possible mechanism for the formation of *N*-[(5-cyano-2-oxoimidazolidin-4-yl)-iminomethyl]-*p*-toluenesulfonamide **3** from the reaction of compound **2** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), is hypothesized. The mechanistic pathway for that reaction is attributed to Ernst Schaumann *et al* [12] as illustrated in Scheme 2.

result is inconsistent with that described by Testa *et al.* [18] for thiation of compounds containing *cis* amino-cyano neighboring group by using Lawesson's reagent.

The infrared spectra of compound **4** showed the appearance of  $\nu$  C=S in the imidazole-2-thione ring at 1158  $\text{cm}^{-1}$  characteristic of the five member thiolactam ring and  $\nu$  C=O



ii) Acetonitrile/under nitrogen atmosphere at 0 °C then 5 mole % of 1,8-diazabicyclo[5.4.0] undec-7-ene/stirred at room temperature for 2 hours.

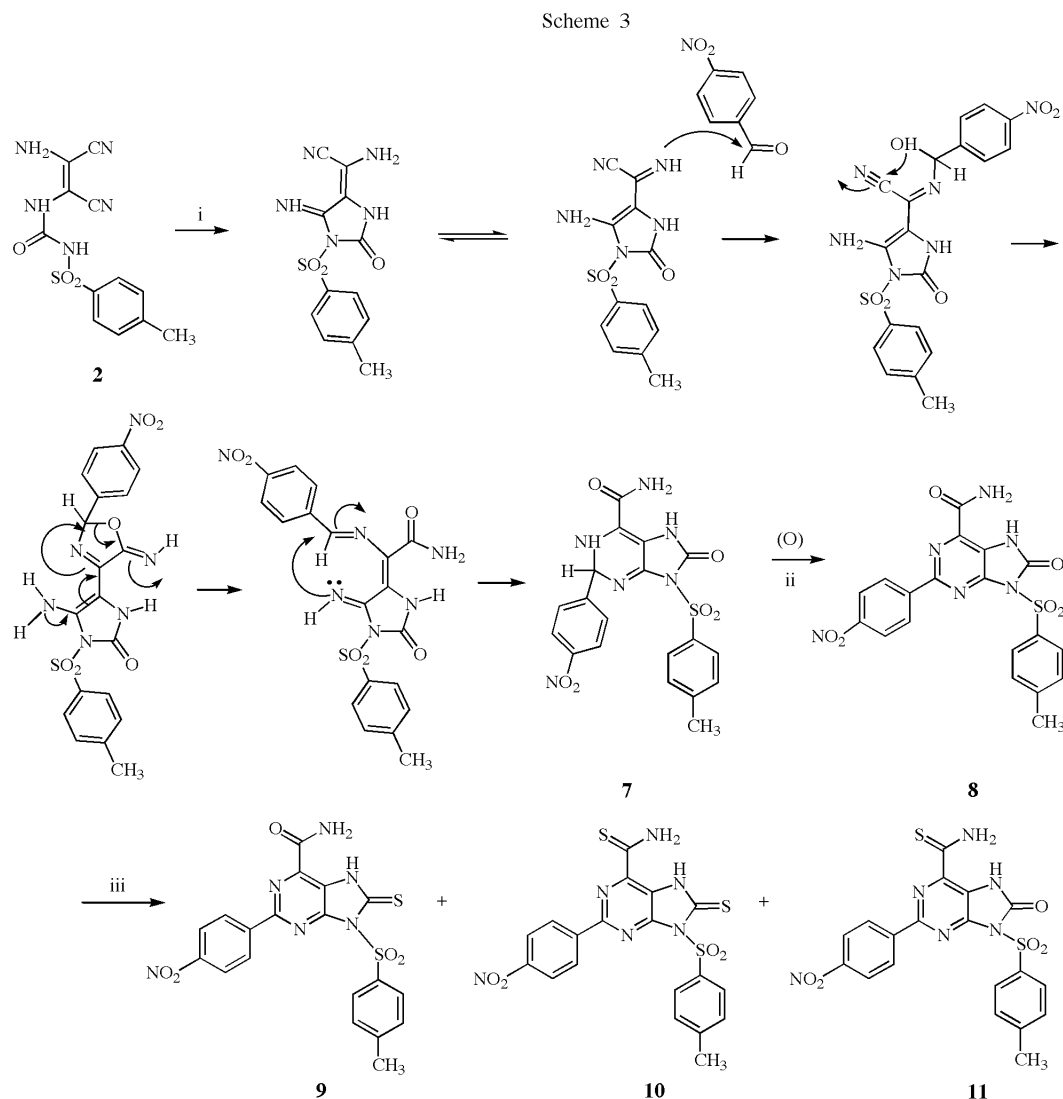
The reaction of compound **3** with Lawesson's reagent [13,14,15,16] was tried in tetrahydrofuran under a nitrogen atmosphere, the corresponding thione-compound **4** was produced in 45% yield with the unexpected by-product of compounds **5** and **6**. The novel compounds **5** and **6** were obtained after chromatographic separation as a yellow crystalline material in (10%) and (15%) yield respectively (Scheme 1). Spot tests [17] confirmed the presence of C=S groups. This

at 1629  $\text{cm}^{-1}$  characteristic of the amide group for compound **4**. In compound **5** appearance  $\nu$  C=S at 1086-1158  $\text{cm}^{-1}$  in imidazole-2-thione ring characteristic of the five member thiolactam ring and thioamide groups as shown in Table 1. In compound **6**,  $\nu$  C=O at 1713  $\text{cm}^{-1}$  is observed consistent with the imidazole-2-one ring and  $\nu$  C=S at 1098-1170  $\text{cm}^{-1}$  characteristic of thioamide group and intense band in the 3200-3441  $\text{cm}^{-1}$  region for ( $\nu$  NH) group.

The <sup>1</sup>H NMR spectra of compounds **4**, **5** and **6** exhibited four singlet signals at δ 8.34, 8.66, 10.14 and 10.86 ppm for NH and NH<sub>2</sub> groups always showed up as a singlet at δ 10.53-10.56 and this seems to be a typically feature of those compounds as shown in Table 1. All bands in the <sup>13</sup>C NMR are sharp, with the signals for (C<sup>i</sup>) of the C=S group around δ 185.3 as shown in Table 3. Compound **2** react with 2-fold molar amount of *p*-nitrobenzaldehyde at room temperature in dry acetonitrile solution in the presence of triethylamine (3 mole equivalents), with the formation of a characteristic orange spot on tlc for the 6-carbamoyl-1,2-dihydropurine **7** derivatives. These can be isolated as air unstable, orange solids **7** as illustrated in Scheme 3 after chromatographic separation. Compound **7** is very unstable both in solution and in the solid state and its color gradually fades to give a

pale orange solid identified as 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide **8**. Thus, it proved impossible to obtain accurate spectroscopic analysis data for compound **7**. In this reaction the 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide **8** was isolated and may arise from the 6-carbamoyl-1,2-dihydropurine **7** by loss of hydrogen under the reaction condition and this due to the oxidation by *p*-nitrobenzaldehyde.

In the study of the thiation of 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide **8** with Lawesson's reagent, refluxing of compound **8** in tetrahydrofuran produced the corresponding compounds **9**, **10** and **11** in low yield, 15, 12, 32% respectively. The infrared spectra of compound **7** as shown in Table 1 showed the appearance of a strong stretching vibration at 1697 and 1636 cm<sup>-1</sup> for two



Reagents and conditions; i) Addition of 2-fold molar amount of 4-nitrobenzaldehyde in the presence of 3-fold molar amount of triethylamine at 0 °C in ethanol then continue stirring at 25 °C for two days; ii) Oxidation by 4-nitrobenzaldehyde; iii) Lawesson's reagent, in tetrahydrofuran reflux for 12 hours.

$\nu$  C=O characteristic of the lactam ring and amide open chain. The  $^1\text{H}$  NMR spectra, exhibited two doublet signals at  $\delta$  6.98 and  $\delta$  8.81 typical of the  $\text{N}^1\text{-H}$  and  $\text{C}_2\text{-H}$  of a 6-carbamoyl-1,2-dihydropurine, clearly indicating the assigned structure. The infrared spectra of compound **8** as shown in Table 1 showed the appearance of a strong stretching vibration at 1705 and 1680  $\text{cm}^{-1}$  for two  $\nu$  C=O characteristic of lactam ring and amide open chain [19]. The  $^1\text{H}$  NMR spectra of compound **8** exhibited a singlet signal at  $\delta$  11.45 typical of  $\text{N}^7\text{-H}$  and two doublet signal at  $\delta$  8.29 and  $\delta$  8.37 for (4H) aromatic protons of 4- $\text{NO}_2\text{C}_6\text{H}_4\text{-R}$  (*p*), at the same coupling constant  $J = 8.7$  Hz, which was clearly indicated to the assigned structure.

The infrared spectra of compound **9** showed the appearance of a strong stretching vibration at 1596  $\text{cm}^{-1}$  for  $\nu$  C=O characteristic of the amide open chain and at 1188  $\text{cm}^{-1}$  for the  $\nu$  C=S characteristic of the thiolactam ring as shown in Table 1. The  $^1\text{H}$  NMR spectra exhibited two singlet signals at  $\delta$  11.35 and 10.6 typical of the  $\text{N}^7\text{-H}$  and ( $-\text{CS-NH}_2$ ) of 7,8-dihydro-2-(4-nitrophenyl)-8-thioxo-9-tosylpurine-6-carboxamide **9**. The infrared spectra of **10** appearance of a strong stretching vibration at 1170 and 1232  $\text{cm}^{-1}$  for two  $\nu$  C=S, characteristic of the thiolactam ring and thioamide open chain as shown in (Table 1).  $^1\text{H}$  NMR spectrum showed two singlet signals at  $\delta$  11.84 and 10.58 typical of  $\text{N}^7\text{-H}$  and ( $-\text{CS-NH}_2$ ) of 7,8-dihydro-2-(4-nitrophenyl)-8-thioxo-9-tosylpurine-6-thiocarboxamide **10**.

The infrared spectra of 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-thiocarboxamide **11** showed the appearance of a strong stretching vibration at 1705 for

$\nu$  C=O characteristic of the lactam ring and sharp intense band at 1169  $\text{cm}^{-1}$  for the  $\nu$  C=S characteristic of the thioamide open chain. The  $^1\text{H}$  NMR spectrum, showing two singlet signal at  $\delta$  11.45 and 10.61 for  $\text{N}^7\text{-H}$  and ( $-\text{CS-NH}_2$ ) of 6-thiocarbamoyl-purine, that clearly indicated to the assigned structure as shown in Table 1.

## EXPERIMENTAL

$^1\text{H}$  NMR spectra were recorded on Varian Plus 300 (300 MHz) or Bruker XL 300 (300 MHz) instruments and the  $^{13}\text{C}$  NMR spectra (with DEPT 135) were measured on a Bruker WP80 or XL 300 instrument. Infrared spectra listed as recorded 'neat' refer to a thin film of material on NaCl disks, and were taken on a Perkin Elmer 1600 FT-IR spectrometer. Melting points were measured on an electrothermal digital melting point apparatus and are uncorrected. The  $R_f$  value reported for TLC analysis was determined on Macherey-Nagel 0.25 mm layer fluorescent UV<sub>254</sub> plates with the indicated solvent system. M-H-W Laboratories (Phoenix, AZ) performed elemental analyses at University of Minho, Braga, Portugal and Cairo University, Egypt.

*N*-[(*Z*)-2-Amino-1,2-dicyanovinylcarbamoyl]-*p*-toluenesulfonamide (**2**).

To a suspension of diaminomaleonitrile **1** (0.68 g, 6.3 mmoles) in acetonitrile (5 mL) under nitrogen atmosphere at 0°, toluenesulfonylisocyanate (1 mL) was added and the whole was stirred for 15 minutes and then at room temperature for 10 minutes. The solid product was collected by filtration, washed with acetonitrile and then ether to give 1.45 g of white powder in 75% yield.

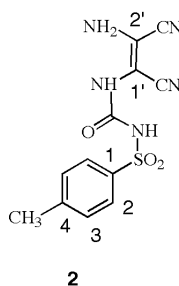
Table 1  
Infrared and  $^1\text{H}$  NMR spectral Data for Compounds **2-11**

Compound	IR	$^1\text{H}$ NMR [deuteriodimethyl sulfoxide]
<b>2</b>	3393, 3201, 2255, 2209, 1645, 1611, 1511, 1457	$\delta = 2.4$ (s, 3H, $-\text{CH}_3$ ), 7.38 (s, 2H, $-\text{NH}_2$ ), 7.41 (d, 2H, $J = 7.8$ Hz, Ar-H), 7.77 (brs, 1H, $-\text{NHCO}$ ), 7.79 (d, 2H, $J = 7.8$ Hz, Ar-H), 11.17 (brs, 1H, CONHTos) ppm
<b>3</b>	3285, 3070, 2231, 1724, 1663, 1621, 1557	$\delta = 2.36$ (s, 3H, $-\text{CH}_3$ ), 7.36 (d, 2H, $J = 8.7$ Hz, Ar), 7.79 (d, 2H, $J = 8.7$ Hz, Ar), 8.41-8.37 (brs, 2H, $-\text{NH}$ ), 11.51 (brs, 2H, NH) ppm
<b>4</b>	3441, 3334, 3299, 3200, 1713, 1629, 1596, 1568.5, 1543, 1170, 1158	$\delta = 2.36$ (s, 3H, $-\text{CH}_3$ ), 7.37 (d, 2H, $J = 8.4$ Hz, Ar), 7.8 (d, 2H, $J = 8.4$ Hz, Ar), 8.34 (s, 1H, $-\text{NH}$ ), 10.14 (s, 1H, $-\text{NH}$ ), 10.95 (s, 1H, NH) ppm
<b>5</b>	3442, 3334, 3200, 1629, 1596, 1568, 1543, 1086, 1158	$\delta = 2.36$ (s, 3H, $-\text{CH}_3$ ), 7.37 (d, 2H, $J = 8.7$ Hz, Ar), 7.8 (d, 2H, $J = 8.7$ Hz, Ar), 8.34 (s, 1H, $-\text{NH}$ ), 8.67 (s, 1H, $-\text{NH}$ ), 10.14 (s, 1H, CONHTos), 10.56 (brs, 2H, $\text{NH}_2$ ), 11.95 (brs, 1H, NH) ppm
<b>6</b>	3441, 3334, 3299, 3200, 1713, 1629, 1596, 1568.5, 1543, 1098, 1170	$\delta = 2.36$ (s, 3H, $-\text{CH}_3$ ), 7.37 (d, 2H, $J = 8.4$ Hz, Ar), 7.8 (d, 2H, $J = 8.4$ Hz, Ar), 8.35 (s, 1H, $-\text{NH}$ ), 8.68 (s, 1H, NH), 10.12 (s, 1H, CONHTos), 10.57 (s, 2H, $\text{NH}_2$ ), 11.97 (s, 1H, NH) ppm
<b>7</b>	3446, 3290, 1697, 1636, 1568	$\delta = 2.32$ (s, 3H, $-\text{CH}_3$ ), 6.98 (brs, 2H, $\text{CONH}_2$ ), 7.25 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.84 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.29 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 8.36 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 9.71 (brs, 1H, NH), 11.35 (brs, 1H, NH) ppm
<b>8</b>	3450, 3158, 1694, 1597	$\delta = 2.27$ (s, 3H, $-\text{CH}_3$ ), 7.25 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.83 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.29 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 8.37 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 8.82 (brs, 1H, NH), 9.25 (brs, 1H, NH), 11.45 (s, 1H, NH) ppm
<b>9</b>	3495, 3244, 1596, 1532, 1344, 1188, 1087	$\delta = 2.32$ (s, 3H, $-\text{CH}_3$ ), 7.43 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.8 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.33 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 8.38 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 10.58 (s, 1H, NH), 11.84 (s, 1H, NH) ppm
<b>10</b>	3495, 3244, 1596, 1532, 1344, 1232, 1170	$\delta = 2.32$ (s, 3H, $-\text{CH}_3$ ), 7.25 (s, 2H, $\text{NH}_2$ ), 7.40 (d, 2H, $J = 8.1$ Hz, Ar-H), 7.98 (d, 2H, $J = 8.1$ Hz, Ar-H), 8.33 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 8.38 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 9.27 (s, 1H, NH) ppm
<b>11</b>	3495, 3244, 1705, 1596, 1532, 1344, 1169, 1087	$\delta = 2.32$ (s, 3H, $-\text{CH}_3$ ), 7.25 (s, 2H, $\text{NH}_2$ ), 7.43 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.8 (d, 2H, $J = 8.4$ Hz, Ar-H), 8.33 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 8.38 (d, 2H, $J = 8.7$ Hz, $\text{NO}_2\text{-C}_6\text{H}_5\text{-H}$ ), 11.45 (s, 1H, NH) ppm

Table 2  
Physical and Elemental Analytical Data for Compounds 2-11

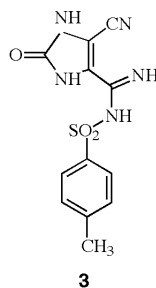
Compound	Melting Point mp(decompd)	Yield%	Molecular Formula	Elemental Analysis [Calcd/found]			
				C	H	N	S
<b>2</b>	>300	75%	C <sub>12</sub> H <sub>11</sub> N <sub>5</sub> SO <sub>3</sub>	47.21/47.12	3.60/3.61	22.95/22.89	10.49/10.56
<b>3</b>	262-263	91%	C <sub>12</sub> H <sub>11</sub> N <sub>5</sub> SO <sub>3</sub>	47.21/47.21	3.60/3.72	22.95/22.82	10.49/10.59
<b>4</b>	280-282	45%	C <sub>12</sub> H <sub>13</sub> N <sub>5</sub> S <sub>2</sub> O <sub>3</sub>	42.47/42.42	3.83/3.81	20.64/20.74	18.88/18.75
<b>5</b>	>300	10%	C <sub>12</sub> H <sub>13</sub> N <sub>5</sub> S <sub>3</sub> O <sub>2</sub>	40.56/40.40	3.66/3.96	19.71/19.63	27.04/27.15
<b>6</b>	>300	16%	C <sub>12</sub> H <sub>11</sub> N <sub>5</sub> S <sub>2</sub> O <sub>3</sub>	42.47/42.42	3.83/3.61	20.64/20.47	18.88/18.05
<b>7</b>	195-198		C <sub>19</sub> H <sub>16</sub> N <sub>6</sub> SO <sub>6</sub>	50.00/50.05	3.50/3.55	18.42/18.48	7.01/7.02
<b>8</b>	205-207	72%	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> SO <sub>6</sub>	50.22/50.18	3.08/3.15	18.50/18.62	7.04/7.32
<b>9</b>	215-217	81%	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>2</sub> O <sub>5</sub>	46.91/47.09	2.88/3.01	17.28/17.11	19.75/19.43
<b>10</b>	212-215	25%	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>3</sub> O <sub>4</sub>	46.91/47.09	2.88/3.01	17.28/17.11	19.75/19.43
<b>11</b>	222-555	32%	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>2</sub> O <sub>5</sub>	48.51/48.46	2.97/3.15	17.87/17.81	13.61/13.62

Table 3  
<sup>13</sup>C Chemical Shifts in Deuteriodimethyl Sulfoxide for *N*-[(*Z*)-2-Amino-1,2-dicyanovinylcarbamoyl]-*p*-toluenesulfonamide **2**



Compound	C1'	C≡N	C≡N	C2'	C=O	C2, C6	C3, C5	C <sub>1</sub> -1	C <sub>1</sub> -4	CH <sub>3</sub>
<b>2</b>	106.1	113.7	117.0	129.7	149.8	127.5	129.5	137.0	144.0	21.0

Table 3  
<sup>13</sup>C Chemical Shifts in Deuteriodimethyl Sulfoxide for *N*-[5-Cyano-2-oxoimidazolidin-4-yl]-iminomethyl]-*p*-toluenesulfonamide (**3**)



Compound	C-5	C≡N	C-4	C=NH	C=O	C2',C6'	C3', C5'	C <sub>1</sub> -1'	C <sub>1</sub> -4'	CH <sub>3</sub>
<b>3</b>	98.0	110.8	126.5	150.93	151.5	126.2	129.3	139.13	142.65	21.0

Recrystallization from ethanol gave colorless powder as shown in Table 2.

*N*-[5-Cyano-2-oxoimidazolidin-4-yl]-iminomethyl]-*p*-toluenesulfonamide (**3**).

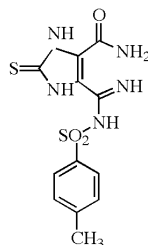
To a suspension of compound **2** (0.35 g, 1.14 mmoles) in acetonitrile (2 mL) under nitrogen atmosphere at 0°, 1,8-Diazabicyclo[5.4.0] undec-7-ene (43 μL, 0.043 g, 0.285 mmole) was added, and then stirred at room temperature for two hours. The solid product was collected by filtration and washed with

acetonitrile to give **3** as a cream-white solid. Recrystallization from ethanol gave colorless powder, mp 262-263°, yield 91% (0.32 g) as shown in Table 2.

Reaction of the *N*-[5-Cyano-2-oxoimidazolidin-4-yl]-iminomethyl]-*p*-toluenesulfonamide (**3**) with Lawesson's reagent.

A mixture of *N*-[5-cyano-2-oxoimidazolidin-4-yl]-iminomethyl]-*p*-toluenesulfonamide (**3**) (0.37 g, 1.23 mmoles) and Lawesson's reagent (0.25 g, 0.616 mmole) was dissolved in tetrahydrofuran (15 ml). The reaction mixture was refluxed for

Table 3  
 $^{13}\text{C}$  Chemical Shifts in Deuteriodimethyl Sulfoxide for 1,3-Dihydro-2-thioxo-4-( $\text{N}^1$ -tosyl)amidino-2H-imidazole-5-carboxamide **4**



Compound	C-5	C=S	C-4	C=NH	C=O	C2', C6'	C3', C5'	C <sub>i</sub> -1'	C <sub>i</sub> -4'	CH <sub>3</sub>
<b>4</b>	126.0	185.2	132.0	150.6	153.7	126.5	129.4	138.4	143.0	21.0

6-10 hours, under nitrogen atmosphere. Evaporation, filtration and successive washing with diethyl ether gave the products **4**, **5** and **6** which were isolated by dry chromatography (ethanol/dichloromethane; 2:8), in the yields 45%, 10% and 15% respectively, as shown in Table 2.

7,8-Dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide (**8**).

A mixture of compound **2** (1.22 g, 4 mmoles) and 4-nitrobenzaldehyde (1.21 g, 8 mmoles) in ethanol (10 ml) was stirred at 0° then triethylamine (3 equivalents) was added dropwise and then keep stirring at room temperature for 26 hours to isolate 1,2-dihydropurine **7**. The reaction mixture was continued stirred for two days later to provide **8** as yellow solid. Compound **8** can be obtained from the reaction of DAMN **1** with tosylisocyanate and 4-nitrobenzaldehyde in ethanol as one pot reaction after stirring three days at room temperature. Recrystallization from ethanol gave yellow crystalline, mp 205-207°, yield 72%, as illustrated in Table 2. Spectral data characteristics were identical with those of the authentic sample in all aspects.

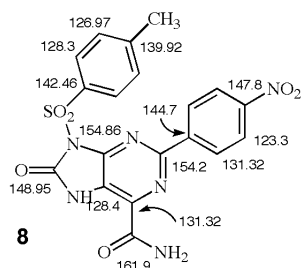


Figure.  $^{13}\text{C}$  Chemical shifts in deuteriodimethyl sulfoxide for 7,8-dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide (**8**).

Reaction of the 7,8-Dihydro-2-(4-nitrophenyl)-8-oxo-9-tosylpurine-6-carboxamide (**8**) with Lawesson's reagent.

A mixture of compound **8** (100 mg, 0.15 mmole) and Lawesson's reagent (60 mg, 0.15 mmole) was dissolved in tetrahydrofuran 10 ml. The reaction mixture was refluxed for 5-7 hours, under nitrogen atmosphere. Evaporation of the solvent and

then filtered off, washed with diethylether to give the corresponding thione-compounds **9**, **10** and **11** which were isolated by dry chromatography (ethanol/dichloromethane; 2:8), in yields 81%, 25% and 32% respectively as shown in Table 2.

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