

# A Convenient Synthesis of New Pentaazacyclopentanaphthalene and Pentaazaphenanthrene Derivates

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Reaction of *N*-{3-cyano-6-[4(5-oxo-2-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-4-phenylpyridin-2-yl}formimidic ethyl ester (**3**) and 3-[4-(3-amino-4-imino-5-phenyl-3,4-dihydropyridin-2-yl)pyrimidin-7-yl]phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (**4**) with different reagents has been investigated and discussed. Some of the obtained compounds were tested for their antimicrobial activity.

**Key words:** Pyridopyrimidine, Malononitrile, Pentaazacyclopentanaphthalene, Pentaazaphenanthrene

## Introduction

Pyridopyrimidines deserve interest due to their biological and pharmacological activities [1–3]. Some of them showed potential antibacterial properties [4], while other derivatives have been used as dihydrofolate reductase inhibitors and as antitumor agents [5, 6]. Also some of these derivatives showed antimicrobial activities [7], diuretic properties [8] and activity against platelet aggregation [9]. In continuation of our previous articles [10–14] directed towards facile synthesis of heterocycles of biological interest, we thought to explore the utility of compounds **3** and **4** as key precursors for synthesis of several hitherto unreported annulated pyridopyrimidines.

## Results and Discussion

Treatment of acetophenone derivatives [15] with benzaldehyde afforded the required starting chalcones **1**. Condensation of equimolar amounts of **1** and malononitrile in the presence of ammonium acetate furnished 2-amino-4-phenylnicotinonitriles **2**. The reaction apparently involves an intramolecular heterocyclization *via* an anticipated Michael-type addition [16, 17] to give the final isolable product **2** (Scheme 1). Treatment of **2** with equimolar amounts of triethyl orthoformate and acetic anhydride afforded the target key reagents **3** [18].

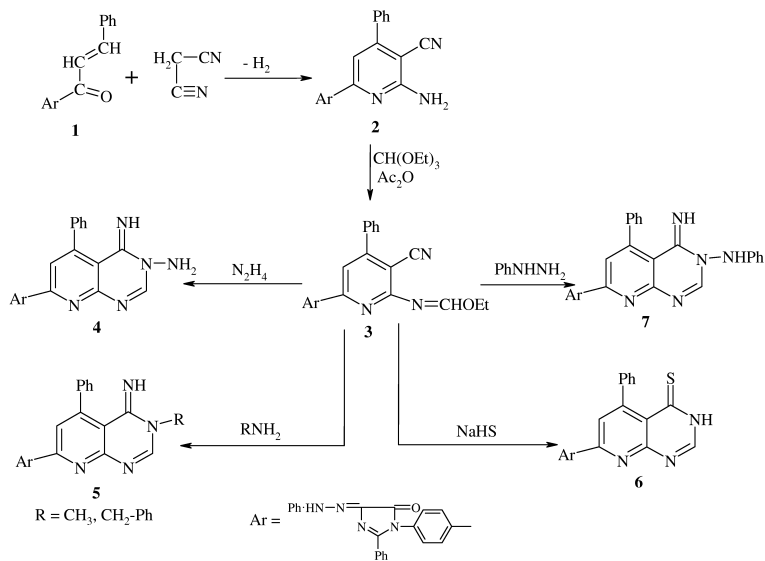
Cyclization of **3** with hydrazine hydrate, methyl or benzyl amine, sodium hydrogen sulfide and finally

with phenylhydrazine furnished the expected pyridopyrimidines **4**, **5a,b**, **6** and **7** as products (Scheme 1). The structure of the above compounds was confirmed by IR, <sup>1</sup>H and <sup>13</sup>C NMR, mass spectra and elemental analysis.

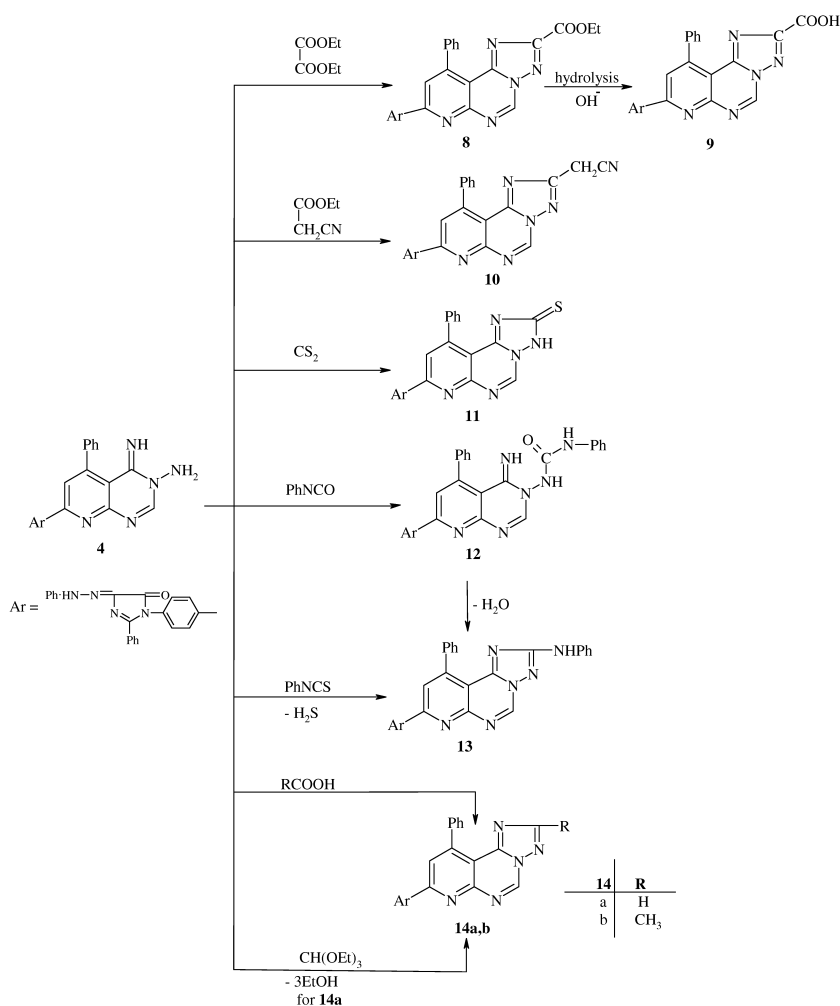
Compound **4** proved to be highly reactive towards various reagents and underwent numerous chemical transformations, resulting in construction of a wide range of annulated and substituted pyridopyrimidine systems. Thus, when equimolar amounts of **4** and diethyl oxalate were refluxed in ethanol, pentaazacyclopenta[a]naphthalene derivative **8** was obtained (Scheme 2). Assignment of structure **8** was based on spectral data, where the IR spectrum of the isolated product displayed the CO absorption band near 1735 cm<sup>-1</sup> corresponding to CO (ester). Also, hydrolysis of the product with sodium hydroxide yielded the corresponding carboxylic acid **9**.

Furthermore, treatment of **4** with ethyl cyanoacetate in absolute ethanol under refluxing condition furnished compound **10**. When compound **4** was allowed to react with carbon disulfide, 2-thioxopentaazacyclopenta[a]naphthalene **11** was isolated in fairly good yield.

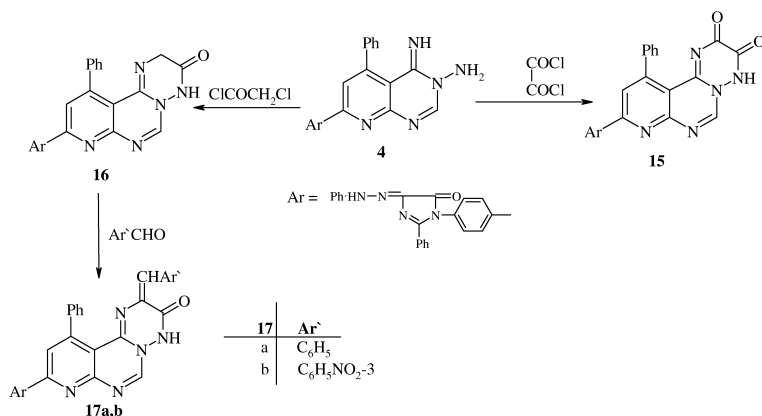
An even more convenient access to 2-phenylamino-1,3,3a,5,6-pentaazacyclopenta[a]naphthalenes **13** was achieved by treatment of pyridopyrimidine **4** with phenyl isocyanate to afford the corresponding phenylurea derivative **12** which in turn yielded compound **13** *via* loss of water molecule. Alternatively, compound **13**



Scheme 1.



Scheme 2.



Scheme 3.

Table 1. Antimicrobial activity.

Compd. No.	Bacillus subtilis		Bacillus cereus		Aspergillus niger		Penicillium spp.	
	A	MIC	A	MIC	A	MIC	A	MIC
4	+	125	+	250	–	–	–	–
5	+	500	+	250	+	125	+	500
6	++	125	++	500	+++	250	++	250
7	+	500	+	250	+	500	+	250
10	–	–	++	250	+	125	+	250
11	++	125	+++	250	++	125	++	250
15	+	250	+	125	+	250	–	–
17a	+	125	–	–	+	250	–	–
17b	++	125	+	125	+	250	–	–

A = antimicrobial activity of tested compounds; MIC = minimum inhibitory concentration; + > 5 mm slightly active; ++ > 7 mm moderately active; +++ > 9 mm highly active.

was prepared through an independent route involving reaction of **4** with an equimolar amount of phenyl isothiocyanate affording a single product, which was found to be identical in all aspects (m.p., mixed m.p., TLC and IR data) with **13**.

On refluxing compound **4** with formic acid or acetic acid **14a** and **14b** were formed respectively. Compound **14a** could be also obtained *via* an alternative route involving refluxing of compound **4** with triethyl orthoformate in dimethyl formamide.

As an extension of the synthetic route, the behaviour of **4** in construction of polyfunctionally substituted pentaazaphenanthrenes was investigated. Thus, treating of **4** with oxalyl chloride in benzene under refluxing condition gave pentaazaphenanthrene-2,3-diones **15** (Scheme 3). Similarly compound **4** was subjected to the reaction with an equimolar amount of chloroacetyl chloride in dry dioxane to furnish the corresponding phenanthrene **16**. The latter was allowed to react with the appropriate aromatic aldehydes in the presence of sodium acetate to afford **17a,b** in good yields.

### Antimicrobial Activity

The antimicrobial activity of some synthesized derivatives towards different strains of various organisms was tested using the hole plate and filter paper method [19]. The tested compounds were dissolved in 10% acetone (v/v), at concentrations of 125, 250 and 500  $\mu\text{g/ml}$ . The results are summarized in Table 1. It should be noted that other pharmacological studies are still in progress.

### Experimental Section

Melting points are uncorrected. IR spectra were recorded on Perkin Elmer 298 Spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on an Varian Gemini 200 MHz and 50 MHz instrument. Mass spectra were recorded on Shimadzu GCMS-QP 1000EX (EI 70 eV) instrument. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F254 (Merck) plates.

$^{13}\text{C}$  NMR values of phenyl groups for compounds **3–17** are the same as in compound **2** with  $\delta \pm 0.1 - 0.3$  ppm.

#### 2-phenyl-3-[4-(3-phenylacryloyl)phenyl]-5-phenylhydrazono-3,5-dihydroimidazol-4-one (**1**)

A mixture of 3-[4-acetylphenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one [**15**] (0.01 mol) and benzaldehyde (0.01 mol) was dissolved in ethanol (100 ml). To the cold stirred mixture, KOH (6.2 g) in water (65 ml) was added dropwise over a period of 30 min and stirring was continued for 3 h. The mixture was left overnight at room temperature then poured onto ice/water. The separated product was filtered off and crystallized from ethanol. Yield (77%), m.p. 180–182  $^{\circ}\text{C}$ . – IR:  $\tilde{\nu} = 3220$  (NH), 1690–1680 (CO), 1620  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta = 6.92, 8.22$  (2d,  $J = 14$  Hz, 2H, 2CH olefinic), 7.35–7.98 (m, 19H, Ar-H), 11.35 (s, 1H, NH, exchangeable). – MS:  $m/z(\%) = 470$  (62)

[M<sup>+</sup>]. – C<sub>30</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>: calcd. C 76.58, H 4.71, N 11.91; found C 76.70, H 4.90, N 11.90.

*2-Amino-6-{4-[5-oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl]phenyl}-4-phenylnicotinonitrile (2)*

A mixture of an equimolar amount from **1** and malononitrile (0.01 mol) was refluxed in ethanol (20 ml) containing ammonium acetate (0.01 mol) for 10 h. The solid product was triturated and crystallized from benzene. Yield (62%), m.p. 301–303 °C. – IR:  $\tilde{\nu}$  = 3360, 3340 (NH<sub>2</sub>), 3200 (NH), 2230 (CN), 1690 (CO), 1610 cm<sup>-1</sup> (C=N). – <sup>1</sup>H NMR (DMSO):  $\delta$  = 3.25 (s, 2H, NH<sub>2</sub>, exchangeable), 7.35–7.98 (m, 20H, Ar-H), 11.33 (s, 1H, NH, exchangeable). – <sup>13</sup>C NMR:  $\delta$  = 110.5 (C-3), 114.4 (CN), 122.3 (C-5), 148.8 (C-4), 155.1 (C=N.NH), 157.3 (C-6), 160.0 (CO), 162.4 (C-2), 165.1 (C-2 imidaz.), 117.3, 119.4, 121.3, 127.2, 127.6, 128.4, 129.8, 129.8, 129.9, 130.0, 130.1, 133.8, 134.2, 137.6, 138.8, 145.6 (C-aromatic). – MS:  $m/z$  (%) = 533 (56) [M<sup>+</sup>]. – C<sub>33</sub>H<sub>23</sub>N<sub>7</sub>O: calcd. C 74.28, H 4.34, N 18.38; found C 74.00, H 4.50, N 18.20.

*N-{3-Cyano-6-[4-(5-oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-4-phenylpyridin-2-yl}formimidic ethyl ester (3)*

To a solution of **2** (0.005 mol) in acetic anhydride (20 ml) triethyl orthoformate (0.005 mol) was added. The reaction mixture was refluxed for 5 h then poured onto cold water. The solid product was collected by filtration, washed with water, dried and crystallized from benzene/petroleum ether (1:1). Yield (86%), m.p. 150–152 °C. – IR:  $\tilde{\nu}$  = 3160 (NH), 2220 (CN), 1685 (CO), 1615 cm<sup>-1</sup> (C=N). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.39 (t,  $J$  = 8.1 Hz, 3H, CH<sub>3</sub>), 4.7 (q,  $J$  = 8.1 Hz, 2H, CH<sub>2</sub>), 7.48–7.99 (m, 20H, Ar-H), 8.23 (s, 1H, olefinic CH), 11.35 (s, 1H, NH, exchangeable). – <sup>13</sup>C NMR:  $\delta$  = 14.8 (CH<sub>3</sub>), 59.7 (OCH<sub>2</sub>), 118.5 (CN), 122.0 (C-5), 130.3 (N=CH), 141.0 (C-3), 148.6 (C-4), 157.5 (C-6), 163.0 (C-2). – MS:  $m/z$  (%) = 589 (53) [M<sup>+</sup>]. – C<sub>36</sub>H<sub>27</sub>N<sub>7</sub>O<sub>2</sub>: calcd. C 73.33, H 4.62, N 16.63; found C 73.10, H 4.70, N 16.60.

*3-[4-(3-Amino-4-imino-5-phenyl-3,4-dihydropyrido[2,3-d]pyrimidin-7-yl)phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (4)*

To a solution of **3** (0.005 mol) in benzene (30 ml) hydrazine hydrate (2 ml in 2 ml H<sub>2</sub>O) was added. The reaction mixture was stirred for 45 min, then allowed to stand overnight whereby the solid product was collected by filtration, dried and crystallized from benzene. Yield (71%), m.p. 221–223 °C. – IR:  $\tilde{\nu}$  = 3390–3320 (NH<sub>2</sub>), 3210–3180 (NH), 1690 (CO), 1620 cm<sup>-1</sup> (C=N). – <sup>1</sup>H NMR (DMSO):  $\delta$  = 5.61 (s, 1H, NH, exchangeable), 7.35–7.99 (m, 20H, Ar-H), 8.23 (s, 1H, pyrimi. H), 11.22 (s, 1H, NH, exchange-

able). – <sup>13</sup>C NMR:  $\delta$  = 121.3 (C-6), 123.0 (C-4a), 139.8 (C-4), 150.2 (C-5), 153.2 (C-2), 155.8 (C-8a), 158.2 (C-7). – MS:  $m/z$  (%) = 575 (41) [M<sup>+</sup>]. – C<sub>34</sub>H<sub>25</sub>N<sub>9</sub>O: calcd. C 70.94, H 4.38, N 21.90; found C 71.10, H 4.40, N 21.80.

*3-[4-(4-Imino-5-phenyl-3-substituted-3,4-dihydropyrido[2,3-d]pyrimidin-7-yl)phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (5a,b)*

*General procedure:* A mixture of **3** (0.001 mol) and the appropriate amine (0.001 mol) in ethanol (20 ml) was refluxed for 12 h. The reaction mixture was poured onto ice water and neutralized with dilute hydrochloric acid. The solid product was filtered off, dried and crystallized from the appropriate solvent.

*3-[4-(4-Imino-3-methyl-5-phenyl-3,4-dihydropyrido[2,3-d]pyrimidin-7-yl)phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (5a)*

Yield (43%), m.p. 140–142 °C (ethanol). – IR:  $\tilde{\nu}$  = 3220–3190 (NH), 1670 cm<sup>-1</sup> (CO). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.51 (s, 3H, CH<sub>3</sub>), 5.80 (s, 1H, NH, exchangeable), 7.37–7.99 (m, 20H, Ar-H), 8.22 (s, 1H, pyrimi. H), 10.92 (s, 1H, NH, exchangeable). – MS:  $m/z$  (%) = 574 (28) [M<sup>+</sup>]. – C<sub>35</sub>H<sub>26</sub>N<sub>8</sub>O: calcd. C 73.16, H 4.56, N 19.50; found C 73.20, H 4.70, N 19.50.

*3-[4-(3-Benzyl-4-imino-5-phenyl-3,4-dihydropyrido[2,3-d]pyrimidin-7-yl)phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (5b)*

Yield (62%), m.p. 190–192 °C (ethanol). – IR:  $\tilde{\nu}$  = 3220–3180 (NH), 1670 cm<sup>-1</sup> (CO). – <sup>1</sup>H NMR (DMSO):  $\delta$  = 5.58 (s, 1H, NH, exchangeable), 6.22 (s, 2H, CH<sub>2</sub>), 7.38–7.98 (m, 25H, Ar-H), 8.22 (s, 1H, pyrimi. H), 11.38 (s, 1H, NH, exchangeable). – <sup>13</sup>C NMR:  $\delta$  = 53.3 (CH<sub>2</sub>), 121.5 (C-6), 123.1 (C-4a), 139.0 (C-4), 150.3 (C-5), 153.3 (C-2), 155.9 (C-8a), 158.3 (C-7). – MS:  $m/z$  (%) = 650 (22) [M<sup>+</sup>]. – C<sub>41</sub>H<sub>30</sub>N<sub>8</sub>O: calcd. C 75.67, H 4.65, N 17.22; found C 75.70, H 4.50, N 17.00.

*2-Phenyl-5-phenylhydrazono-3-[4-(5-phenyl-4-thioxo-3,4-dihydropyrido[2,3-d]pyrimidin-7-yl)phenyl]-3,5-dihydroimidazol-4-one (6)*

To a solution of **3** (0.001 mol) in absolute ethanol (20 ml) sodium hydrogen sulfide (0.0011 mol) was added. The reaction mixture was refluxed for 7 h then poured onto ice. The formed solid product was collected by filtration, dried and crystallized from AcOH. Yield (45%), m.p. 191–192 °C. – IR:  $\tilde{\nu}$  = 3210–3190 (NH), 1680 (CO), 1610 (C=N), 1310 cm<sup>-1</sup> (CS). – <sup>1</sup>H NMR (DMSO):  $\delta$  = 5.91 (s, 1H, NH, exchangeable), 7.29–7.82 (m, 20H, Ar-H), 8.60 (s, 1H, pyrimi.), 10.91 (s, 1H, NH, exchangeable). – <sup>13</sup>C NMR:  $\delta$  =

121.2 (C-6), 123.1 (C-4a), 150.4 (C-5), 154.0 (C-2), 156.1 (C-8a), 158.3 (C-7), 173.2 (C-4). – MS:  $m/z$  (%) = 577 (44)  $[M^+]$ . –  $C_{34}H_{23}N_7OS$ : calcd. C 70.69, H 4.01, N 16.97; found C 70.90, H 4.00, N 17.00.

*3-[4-(4-Imino-3-phenylamino-5-phenyl-3,4-dihydro-pyrido[2,3-d]pyrimidin-7-yl)phenyl]-2-phenyl-5-phenyl-hydrazono-3,5-dihydroimidazol-4-one (7)*

To a solution of **3** (0.001 mol) in ethanol (20 ml) phenylhydrazine (0.001 mol) was added. The reaction mixture was refluxed for 3 h then poured onto ice water, filtered off, dried and crystallized from benzene. Yield (58%), m.p. 203–205 °C. – IR:  $\tilde{\nu}$  = 3210–3170 (NH), 1680 (CO), 1610  $cm^{-1}$  (C=N). –  $^1H$  NMR (DMSO):  $\delta$  = 5.56 (s, 1H, NH, exchangeable), 7.39–7.98 (m, 25H, Ar-H), 8.21 (s, 1H, pyrimidi. H), 9.93, 10.25 (2s, 2H, 2NH, exchangeable). – MS:  $m/z$  (%) = 651 (18)  $[M^+]$ . –  $C_{40}H_{29}N_9O$ : calcd. C 73.72, H 4.49, N 19.34; found C 73.90, H 4.30, N 19.40.

*7-{4-[5-Oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl]phenyl}-9-phenyl-1,3,3a,5,6-pentaazacyclopenta[a]naphthalene-2-carboxylic acid ester (8)*

A mixture of **4** (0.001 mol) and diethyl oxalate (0.001 mol) in absolute ethanol (30 ml) was refluxed for 5 h. After cooling the formed solid product was filtered off, dried and crystallized from ethanol. Yield (77%), m.p. 251–253 °C. – IR:  $\tilde{\nu}$  = 3180 (NH), 1735 (CO ester), 1690 (CO amide), 1625  $cm^{-1}$  (C=N). –  $^1H$  NMR (DMSO):  $\delta$  = 1.37 (t,  $J$  = 8.2 Hz, 3H,  $CH_3$ ), 4.36 (q,  $J$  = 8.2 Hz, 2H,  $CH_2$ ), 7.47–7.99 (m, 20H, Ar-H), 9.22 (s, 1H, pyrimidi. H), 10.98 (s, 1H, NH, exchangeable). –  $^{13}C$  NMR:  $\delta$  = 14.4 ( $CH_3$ ), 62.4 ( $CH_2$ ), 121.2 (C-8), 123.0 (C-9a), 148.6 (C-9b), 150.4 (C-9), 156.2 (C-5a), 156.8 (C-2), 158.2 (C-7), 158.8 (C-4), 167.3 (CO). – MS:  $m/z$  (%) = 657 (44)  $[M^+]$ . –  $C_{38}H_{27}N_9O_3$ : calcd. C 69.40, H 4.14, N 19.17; found C 69.30, H 4.20, N 19.20.

*Preparation of 9 from 8*

A mixture of **8** (0.001 mol) and sodium hydroxide 10% (20 ml) was refluxed for 5 h. After cooling the reaction mixture was poured onto ice water and neutralized with dilute hydrochloric acid. The formed solid product was filtered off, dried and crystallized from benzene. Yield (54%), m.p. 180–181 °C. – IR:  $\tilde{\nu}$  = 3470 (OH), 1705 (CO acid), 1685  $cm^{-1}$  (CO amide). –  $^1H$  NMR (DMSO):  $\delta$  = 7.38–7.87 (m, 20H, Ar-H), 9.22 (s, 1H, pyrimidi. H), 10.81, 12.9 (2s, 2H, NH, OH, exchangeable). –  $^{13}C$  NMR:  $\delta$  = 122.2 (C-8), 123.1 (C-9a), 148.9 (C-9b), 150.4 (C-9), 156.4 (C-5a), 158.1 (C-7), 158.3 (C-2), 158.6 (C-4), 174.5 (CO). – MS:  $m/z$  (%) = 629 (42)  $[M^+]$ . –  $C_{36}H_{23}N_9O_3$ : calcd. C 68.67, H 3.68, N 20.02; found C 68.70, H 3.50, N 20.00.

*7-[4-(5-Oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-9-phenyl-1,3,3a,5,6-pentaazacyclopenta[a]naphthalene-2-acetonitrile (10)*

A mixture of **4** (0.005 mol) and ethyl cyanoacetate (0.01 mol) in absolute ethanol (30 ml) was refluxed for 7 h. The formed solid product was filtered off, dried and crystallized from ethanol. Yield (56%), m.p. 205–206 °C. – IR:  $\tilde{\nu}$  = 3160 (NH), 2240 (CN), 1695 (CO amide), 1620  $cm^{-1}$  (C=N). –  $^1H$  NMR (DMSO):  $\delta$  = 4.20 (s, 2H,  $CH_2$ ), 7.35–7.99 (m, 20H, Ar-H), 9.26 (s, 1H, pyrimidi. H), 11.32 (s, 1H, NH, exchangeable). –  $^{13}C$  NMR:  $\delta$  = 22.4 ( $CH_2$ ), 115.2 (CN), 120.6 (C-8), 122.1 (C-9a), 148.3 (C-9b), 150.2 (C-9), 157.0 (C-5a), 158.2 (C-7), 158.4 (C-4), 160.8 (C-2). – MS:  $m/z$  (%) = 624 (33)  $[M^+]$ . –  $C_{37}H_{24}N_{10}O$ : calcd. C 71.14, H 3.87, N 22.42; found C 71.00, H 3.90, N 22.60.

*2-Phenyl-5-phenylhydrazono-3-[4-(9-phenyl-2-thioxo-2,3-dihydro-1,3,3a,5,6-pentaazacyclopenta[a]naphthalene-7-yl)phenyl]-3,5-dihydroimidazol-4-one (11)*

To a solution of **4** (0.001 mol) in absolute ethanol (50 ml) excess of carbon disulfide (5 ml) was added. The reaction mixture was heated on water bath for 4 h. The formed solid product was collected by filtration, dried and crystallized from benzene/ethanol (3:1). Yield (65%), m.p. 190–192 °C. – IR:  $\tilde{\nu}$  = 3260–3200 (NH), 1692 (CO), 1610 (C=N), 1250  $cm^{-1}$  (CS). –  $^1H$  NMR (DMSO):  $\delta$  = 7.39–7.96 (m, 20H, Ar-H), 8.70 (s, 1H, NH, exchangeable), 9.27 (s, 1H, pyrimidi. H), 11.32 (s, 1H, NH exchangeable). – MS:  $m/z$  (%) = 617 (22)  $[M^+]$ . –  $C_{35}H_{23}N_9OS$ : calcd. C 68.06, H 3.75, N 20.41; found C 68.20, H 3.60, N 20.50.

*N-{4-Imino-7-[4-(5-oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)-phenyl]-5-phenyl-4H-pyrido[2,3-d]pyrimidin-3-yl}-3-phenylurea (12)*

To a solution of **4** (0.001 mol) in absolute ethanol (30 ml) phenyl isocyanate (0.001 mol) was added, then the reaction mixture was refluxed for 12 h. After cooling the formed precipitate was filtered off, dried and crystallized from benzene. Yield (58%), m.p. 268–269 °C. – IR:  $\tilde{\nu}$  = 3490–3200 (OH, NH), 1690–1680  $cm^{-1}$  (CO). –  $^1H$  NMR (DMSO):  $\delta$  = 5.56, 6.35, 7.32 (3s, 3H, 3NH, exchangeable), 7.36–8.1 (m, 25H, Ar-H), 9.23 (s, 1H, pyrimidi. H), 11.12 (s, 1H, NH, exchangeable). –  $^{13}C$  NMR:  $\delta$  = 121.6 (C-6), 123.3 (C-4a), 141.0 (C-4), 150.5 (C-5), 153.4 (C-2), 155.8 (C-8a), 158.9 (C-7), 162.8 (CO). – MS:  $m/z$  (%) = 694 (20)  $[M^+]$ . –  $C_{41}H_{30}N_{10}O_2$ : calcd. C 70.88, H 4.35, N 20.16; found C 70.80, H 4.40, N 20.30.

*2-Phenyl-5-phenylhydrazono-3-[4-(9-phenyl-2-phenylamino-1,3,3a,5,6-penta-azacyclopenta[a]naphthalene-7-yl)phenyl]-3,5-dihydroimidazol-4-one (13)*

*Method A:* To a solution of **4** (0.001 mol) in absolute ethanol (30 ml) phenyl isothiocyanate (0.001 mol) was

added. The reaction mixture was refluxed for 20 h then left aside at room temperature whereby the solid product was collected by filtration, dried and crystallized from ethanol. Yield (53%), m.p. 240–243 °C. – IR:  $\tilde{\nu}$  = 3250–3200 (NH), 1690 (CO), 1620  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 7.35 (s, 1H, NH, exchangeable), 7.41–7.98 (m, 25H, Ar-H), 9.25 (s, 1H, pyrimi. H), 11.11 (s, 1H, NH, exchangeable). – MS:  $m/z$  (%) = 676 (38) [ $\text{M}^+$ ]. –  $\text{C}_{41}\text{H}_{28}\text{N}_{10}\text{O}$ : calcd. C 72.77, H 4.17, N 20.70; found C 72.80, H 4.20, N 20.60.

**Method B:** To a solution of **12** (0.001 mol) in ethanol (30 ml) concentrated hydrochloric acid (3 ml) was added, then the reaction mixture was refluxed for 4 h. After cooling the formed precipitate was collected by filtration, washed, dried and crystallized.

*3-[4-(2-Alkyl-9-phenyl-1,3,3a,5,6-pentaazacyclopenta[a]-naphthalene-7-yl)phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (14a,b)*

#### General procedure

##### Method A

A mixture of **4** (0.001 mol) and excess of the appropriate carboxylic acid (15 ml) was refluxed for 10 h. After cooling and dilution with water the precipitate was filtered off, dried and crystallized from the appropriate solvent to give **14a,b**.

*2-Phenyl-5-phenylhydrazono-3-[4-(9-phenyl-1,3,3a,5,6-pentaazacyclopenta[a]naphthalene-7-yl)phenyl]-3,5-dihydroimidazol-4-one (14a)*

Yield (67%), m.p. 270–272 °C (benzene). – IR:  $\tilde{\nu}$  = 3200 (NH), 1685 (CO), 1620–1615  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 7.38–8.20 (m, 21H, Ar-H + triazine H), 9.31 (s, 1H, pyrimi. H), 11.02 (s, 1H, NH, exchangeable). –  $^{13}\text{C}$  NMR:  $\delta$  = 121.0 (C–8), 122.0 (C–9a), 139.3 (C–2), 148.0 (C–9b), 150.2 (C–9), 156.6 (C–5a), 157.9 (C–7), 158.7 (C–4). – MS:  $m/z$  (%) = 585 (23) [ $\text{M}^+$ ]. –  $\text{C}_{35}\text{H}_{23}\text{N}_9\text{O}$ : calcd. C 71.78, H 3.96, N 21.53; found C 71.80, H 4.10, N 21.50.

*3-[4-(2-Methyl-9-phenyl-1,3,3a,5,6-pentaazacyclopenta[a]-naphthalene-7-yl)phenyl]-2-phenyl-5-phenylhydrazono-3,5-dihydroimidazol-4-one (14b)*

Yield (63%), m.p. 236–238 °C (benzene). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 2.6 (s, 3H,  $\text{CH}_3$ ), 7.38–8.0 (m, 20H, Ar-H), 9.22 (s, 1H, pyrimi.H), 11.22 (s, 1H, NH, exchangeable). –  $^{13}\text{C}$  NMR:  $\delta$  = 22.1 ( $\text{CH}_3$ ), 121.1 (C–8), 122.2 (C–9a), 136.9 (C–2), 148.1 (C–9b), 149.8 (C–9), 156.6 (C–5a), 157.7 (C–7), 158.2 (C–4). – MS:  $m/z$  (%) = 599 (31) [ $\text{M}^+$ ]. –  $\text{C}_{36}\text{H}_{25}\text{N}_9\text{O}$ : calcd. C 72.11, H 4.20, N 21.02; found C 72.30, H 4.30, N 21.00.

##### Method B

Equimolar amounts from **4** and triethyl orthoformate (0.005 mol) were refluxed in DMF for 8 h. The solvent was evaporated *in vacuo* and the resulting solid product was crystallized to give **14a**.

*7-[4-(5-Oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-5-phenyl-1,4,8,9,10a-pentaazaphenanthrene-2,3-dione (15)*

To a solution of **4** (0.003 mol) in dry benzene (30 ml) oxalyl chloride (3 ml) was added and the reaction mixture was refluxed for 9 h. After cooling the solid product was collected by filtration, dried and crystallized from acetic acid. Yield (62%), m.p. 236–238 °C. – IR:  $\tilde{\nu}$  = 3400–3250 (OH, NH), 1690–1680 (CO), 1622  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 7.39 (s, 1H, NH, exchangeable), 7.55–7.76 (m, 20H, Ar-H), 8.21 (s, 1H, pyrimi. H), 11.29 (s, 1H, NH, exchangeable). –  $^{13}\text{C}$  NMR:  $\delta$  = 122.3 (C–6), 123.0 (C–4b), 150.1 (C–5), 150.7 (C–4a), 154.0 (CO), 156.2 (C–8a), 157.8 (C–7), 158.3 (CO), 158.9 (C–10). – MS:  $m/z$  (%) = 629 (61) [ $\text{M}^+$ ]. –  $\text{C}_{36}\text{H}_{23}\text{N}_9\text{O}_3$ : calcd. C 68.67, H 3.68, N 20.02; found C 68.80, H 3.70, N 20.00.

*7-[4-(5-Oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-5-phenyl-3H-1,4,8,9,10a-pentaazaphenanthren-2-one (16)*

A mixture of **4** (0.004 mol) and chloroacetyl chloride (0.004 mol) in dry dioxane (40 ml) was allowed to stand at room temperature overnight. The formed precipitate was filtered off, dried and crystallized from dioxane. Yield (66%), m.p. 281–283 °C. – IR:  $\tilde{\nu}$  = 3370–3220 (OH, NH), 1690–1685 (CO), 1615  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 5.21 (s, 2H,  $\text{CH}_2$ ), 7.41 (s, 1H, NH, exchangeable), 7.56–7.99 (m, 20H, Ar-H), 8.22 (s, 1H, pyrimi.H), 11.26 (s, 1H, NH, exchangeable). –  $^{13}\text{C}$  NMR:  $\delta$  = 55.8 ( $\text{CH}_2$ ), 121.8 (C–6), 123.1 (C–4b), 150.2 (C–5), 150.3 (C–4a), 154.4 (CO), 156.8 (C–8a), 157.6 (C–7), 158.8 (C–10). – MS:  $m/z$  (%) = 615 (51) [ $\text{M}^+$ ]. –  $\text{C}_{36}\text{H}_{23}\text{N}_9\text{O}_2$ : calcd. C 70.23, H 4.09, N 20.48; found C 70.40, H 4.10, N 20.50.

*3-Arylidene-7-[4-(5-oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-5-phenyl-3H-1,4,8,9,10a-pentaazaphenanthren-2-one (17a,b)*

##### General procedure

A mixture of **4** (0.002 mol) and the appropriate aromatic aldehyde (0.002 mol) was refluxed for 6 h in acetic acid (20 ml) containing anhydrous sodium acetate (1 g). The reaction mixture left aside whereby the solid product was collected by filtration, washed thoroughly with water, dried and crystallized from the appropriate solvent.

*3-Benzylidene-7-[4-(5-oxo-2-phenyl-4-phenylhydrazono-4,5-dihydro-imidazol-1-yl)phenyl]-5-phenyl-3H-1,4,8,9,10a-pentaazaphenanthren-2-one (17a)*

Yield (56%), m.p. 265–267 °C (ethanol). – IR:  $\tilde{\nu}$  = 3390–3200 (OH, NH), 1685 (CO), 1620  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 7.53–7.98 (m, 25H, Ar-H), 7.81 (s, 1H, NH, exchangeable), 8.15 (s, 1H, olefinic H), 8.22 (s, 1H, pyrimi.H), 10.39 (s, 1H, NH, exchangeable). –  $^{13}\text{C}$  NMR:  $\delta$  = 121.9 (C–6), 123.2 (C–4b), 128.0 (CHAr'), 134.3 (C=CHAr'), 150.3 (C–5), 150.5 (C–4a), 154.3 (CO), 156.9 (C–8a), 158.0 (C–7), 159.2 (C–10), 127.7, 129.8, 130.3, 133.9 (C–Ar'). – MS:  $m/z$  (%) = 703 (51) [ $\text{M}^+$ ]. –  $\text{C}_{43}\text{H}_{29}\text{N}_9\text{O}_2$ : calcd. C 73.39, H 4.15, N 17.91; found C 73.50, H 4.30, N 17.90.

*3-(3-Nitrobenzylidene)-7-[4-(5-oxo-2-phenyl-4-phenylhydrazono-4,5-dihydroimidazol-1-yl)phenyl]-5-phenyl-3H-1,4,8,9,10a-pentaazaphenanthren-2-one (17b)*

Yield (76%), m.p. 292–294 °C (ethanol). – IR:  $\tilde{\nu}$  = 3390–3210 (OH, NH), 1690 (CO), 1620  $\text{cm}^{-1}$  (C=N). –  $^1\text{H}$  NMR (DMSO):  $\delta$  = 7.53–7.99 (m, 24H, Ar-H), 7.82 (s, 1H, NH, exchangeable), 8.16 (s, 1H, olefinic H), 8.22 (s, 1H, pyrimi.H), 10.38 (s, 1H, NH, exchangeable). – MS:  $m/z$  (%) = 748 (21) [ $\text{M}^+$ ]. –  $\text{C}_{43}\text{H}_{28}\text{N}_{10}\text{O}_4$ : calcd. C 68.98, H 3.77, N 18.71; found C 68.80, H 3.90, N 18.60.

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