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Efficient route to benzo[4,5]imidazo[2,1-*a*]phthalazines

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Abstract—Benzo[4,5]imidazo[2,1-*a*]phthalazines have been obtained from various *o*-nitrophenylhydrazines through different 2-(2-nitrophenyl)-1,2-dihydro-1-phthalazinones as intermediates using an elaborated advanced procedure. An activated chlorine atom in 2-nitrophenyl moiety of the latter is able to undergo nucleophilic substitution for secondary alicyclic amines yielding novel substituted phthalazinones. Their one-pot reduction and cyclodehydration yield a series of novel substituted benzo[4,5]imidazo[2,1-*a*]phthalazines.

1. Introduction

Benzo[4,5]imidazo[2,1-*a*]phthalazine (BIPH) formerly described in 1937 by Rowe et al.[1] is a tetracyclic aza-heterocycle isoelectronic to aromatic hydrocarbon viz. chrysene. Three derivatives of this heterocycle including that of unsubstituted BIPH have been obtained (Scheme 1).

Diazotized benzene substituted *o*-nitroanilines have been transformed into the salts of 2-naphthol-1-sulfonic acid. A series of transformations involving a scission of naphthalene cycle and formation of phthalazine cycle result in formation of 3-(2-nitrophenyl)-substituted phthalazinium-1-olate. The latter have been reduced with aqueous sodium sulfide followed by rearrangement and subsequent cyclization on treating with dilute HCl at 180 °C in a sealed tube.

The structure of BIPHs has been proved by direct synthesis using alternative route (Scheme 2).[1] For two subsequent cyclizations have been used the same conditions: aqueous sodium sulfide, then dilute HCl at 180 °C in a sealed tube.

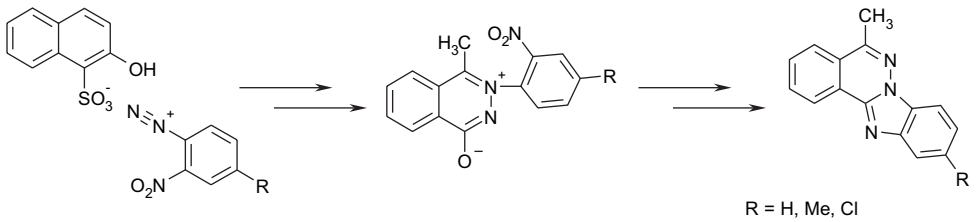
Later BIPHs have been also obtained[2] from *o*-aminophenol (Scheme 3). Substituted BIPH possess slight antihypertensive and antiinflammatory activities;[2] however, neither further investigations have been performed.

2. Results and discussion

In our preliminary communication[3] we have briefly described the synthesis of several newly substituted BIPH. In the present work we would like to present their syntheses more comprehensively.

We have worked out more general but rather brief synthetic route yielding BIPHs by incorporating various substituents in heterocyclic moiety. We have found it attractive to use *o*-nitrophenylhydrazines for synthesis of phthalazine cycle. In order to make this scheme more practicable we have to solve several problems as follows:

1. To elaborate a general procedure of cyclization of 2-acylbenzoic acids with 2-nitrophenylhydrazines yielding 2-nitrophenyl substituted phthalazin-1-ones;



Scheme 1.

Keywords: Nucleophilic substitution; Phthalazinone; Cyclodehydration; Benzimidazole.
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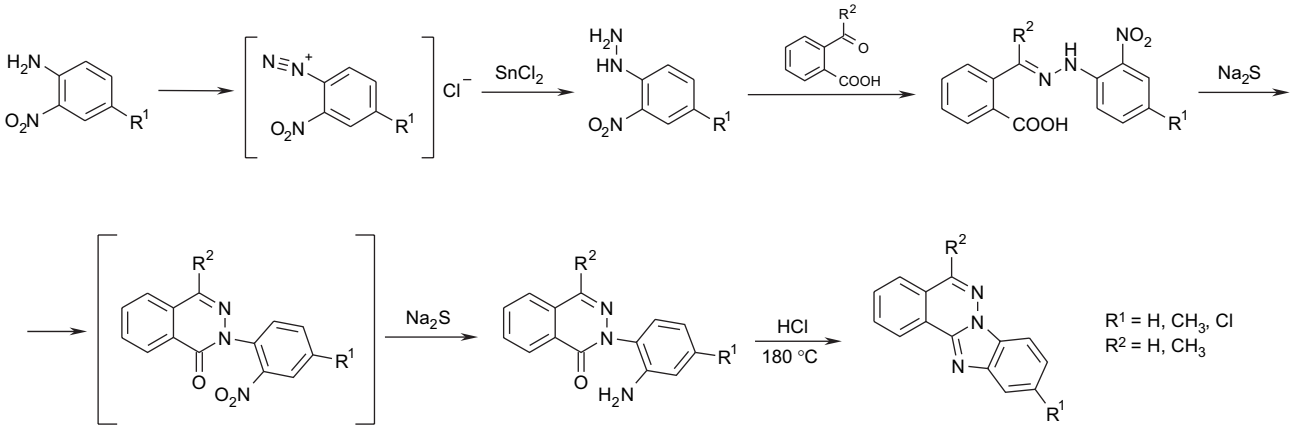
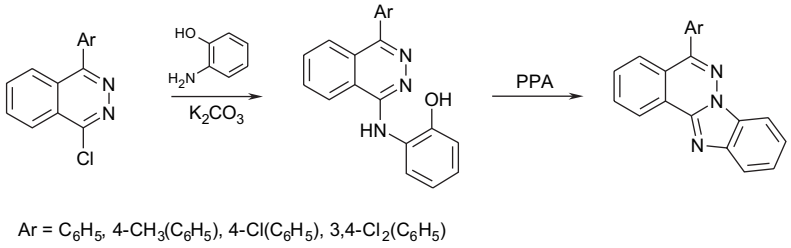


Scheme 2.

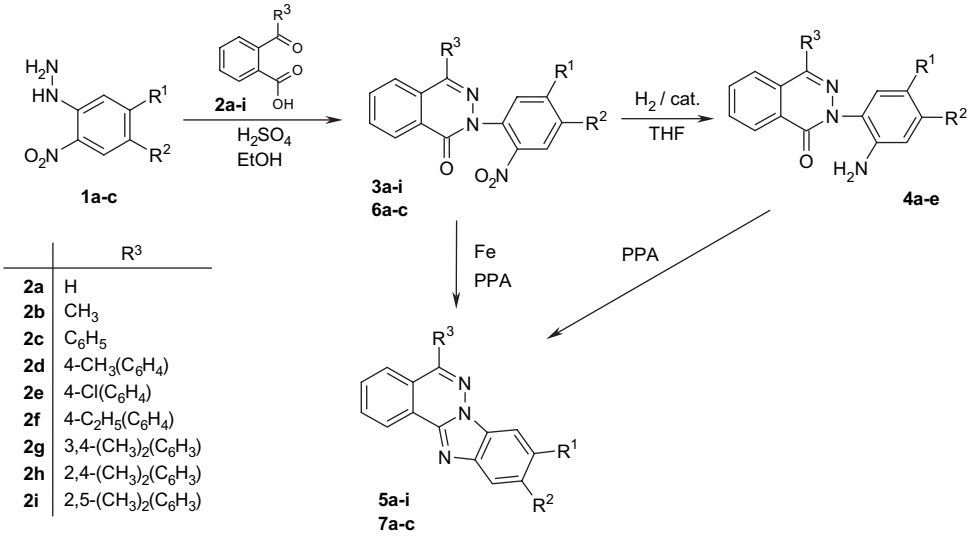


Scheme 3.

2. To perform nucleophilic substitution of chlorine atom in 2-nitro-5-chlorophenyl moiety of phthalazin-1-one with alkylamines;
3. To work out a procedure of reduction of *o*-nitro group into amino group;
4. To select conditions for cyclization of 2-aminophenylphthalazinones yielding BIPH.

The outlined scheme is shown in Scheme 4.

As to the initial compounds many of the acylbenzoic acids are readily available. A number of 2-nitrophenylhydrazines available are much more limited. These hydrazines are usually obtained by reduction of diazonium derivatives of the relative anilines or by substitution of halogen atom in activated arylhalogenides with hydrazine hydrate. 2-Nitro-5-chlorophenylhydrazine **1a** is easily available by the reaction of hydrazine with 3,4-dinitrochlorobenzene.[4,5] Its subsequent condensation with *o*-acylbenzoic acid **2** and subsequent cyclization of the reaction product may yield phthalazinone **3** incorporating chlorine atom in *para*-position to nitro group. This chlorine atom is activated enough to undergo the second nucleophilic substitution thus making it possible to introduce a wide range of new substituents.



	R^3
2a	H
2b	CH_3
2c	C_6H_5
2d	4-$CH_3(C_6H_4)$
2e	4-$Cl(C_6H_4)$
2f	4-$C_2H_5(C_6H_4)$
2g	3,4-$(CH_3)_2(C_6H_3)$
2h	2,4-$(CH_3)_2(C_6H_3)$
2i	2,5-$(CH_3)_2(C_6H_3)$

Scheme 4.

Formerly interaction of nitrophenylhydrazines with *o*-acylbenzoic acids has drawn a little attention.[6–9] In the literature there are only limited examples of ring formation involving *o*-nitrosubstituted phenylhydrazines, which are especially difficult for cyclizations.[1,8,10] Experimental procedures used by Rowe et al.[1] for synthesis of 2-(2-nitrophenyl)-1-phthalazinones and subsequent reduction of nitro group are inconvenient and hardly scalable.

To our knowledge hydrazine **1a** has never been involved into reaction with acylbenzoic acids. We have tried to perform this reaction with acid **2** under ordinary conditions but only intermediate hydrazones were isolated. In searching for appropriate conditions we have found that a relatively good yield may be achieved by boiling reagents in ethanol–sulfuric acid mixture (2:1 by volume). This mixture is boiling in the range from 100 to 120 °C, which happens to be optimal for cyclization. However, on more prolonged boiling side reactions lowering the yield of phthalazine **3** (Table 1) become pronounced.

Nitro groups of several phthalazines from this series have been catalytically reduced into relative anilines **4a–e** (Table 1) by gaseous hydrogen in THF solution. The reduction has been performed fast and with quantative yields on using Raney nickel or palladium on carbon. Under these conditions the solubility of the substituted phenylenediamine **4** has been noticeably decreased on the enhancement of the molecular mass of the substituent in position 4 causing their crystallization from the reaction mixture and catalyst's deactivation.

In the next stage (Scheme 4) we have used polyphosphoric acid (PPA) as highly efficient dehydrating agent lacking side reactions unlike sulfuric acid. Moreover at high temperatures PPA is an effective solvent for organic compounds especially for those nitrogen incorporating. A short-term heating of aniline **4** in PPA solution leads to cyclization of *o*-amino group with carbonyl group yielding BIPHs **5a–i**. This reaction is similar to a well-known scheme of synthesis of benzimidazoles using *N*-acyl-*o*-phenylenediamines.[11]

Under optimal conditions (100–130 °C) only selective dehydration (as observed by TLC), with formation of BIPHs **5a–i**, occurs with high yield. As we don't observe any side products the almost pure BIPHs have been isolated by water dilution of the reaction mixture with its subsequent neutralization to pH 7.0. Analytically pure products have been obtained on their recrystallization from suitable solvent.

We have succeeded in overcoming the problem of poor solubility of the initial aniline **4** in THF as well as that of simplifying the synthesis of the BIPHs by carrying it out without isolation of reduction intermediates. To start this transformation we have tried to use PPA as a solvent. However, we haven't succeeded in promoting catalytic reduction in these conditions. Due to high viscosity of PPA even at elevated temperatures we couldn't achieve satisfactory stirring of the reaction mixture. In order to make the synthesis more convenient and fast we have used chemical reduction with iron powder–PPA mixture. To our knowledge formerly this combination hasn't been ever used for reduction of nitro groups.

As would be expected the reaction under consideration occurs as two-stage one-pot synthesis yielding BIPH **5**. The substances obtained proved to be identical with that of obtained from two-stage synthesis.

The validity of synthetic route elaborated has been tested by synthesis of BIPH **7** starting from 2-nitrophenylhydrazine **1b** and 2,4-dinitrophenylhydrazine **1c**. The latter has been used for synthesis of phthalazinones **6a–c** (Scheme 4) in the ethanol–sulfuric acid mixture with increased proportion of the acid. These phthalazinones especially that of **6b** possess the minor solubility from all the series involved. Thus we couldn't hydrogenate them in THF solution. In spite of their moderate solubility in hot PPA we have obtained BIPH **7** with high yields. In the case of phthalazinone **6b** both the nitro groups are reduced yielding BIPH with amino group in 10 position making it possible to extend the range of substituted BIPH through its reactions.

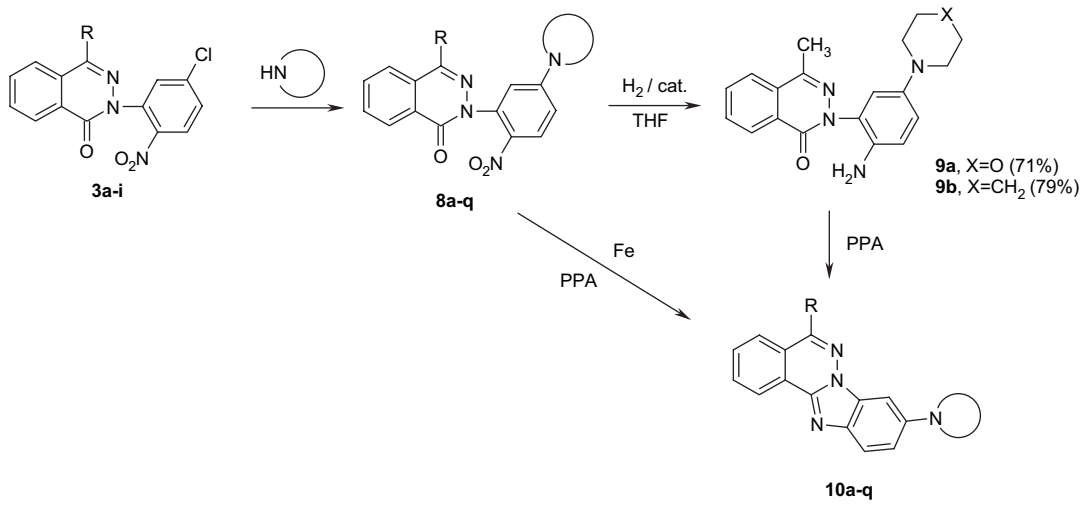
The chlorine atom in the side benzene ring of the compound **3** is activated enough for nucleophilic substitution with dialkylamines (Scheme 5).

It was found that highly basic amines like morpholine, pyrrolidine, piperidine, and piperazine may easily react with

Table 1

No.	R^1	R^2	R^3	Yield,[a] %	No.	R^1	R^2	R^3	Yield, %
3a	Cl	H	H	47	**5a**	Cl	H	H	na[b]/68[c]
3b	Cl	H	CH_3	70	**5b**	Cl	H	CH_3	61/58
3c	Cl	H	C_6H_5	58	**5c**	Cl	H	C_6H_5	64/69
3d	Cl	H	4-$CH_3(C_6H_4)$	60	**5d**	Cl	H	4-$CH_3(C_6H_4)$	na/55
3e	Cl	H	4-$Cl(C_6H_4)$	53	**5e**	Cl	H	4-$Cl(C_6H_4)$	52/50
3f	Cl	H	4-$C_2H_5(C_6H_4)$	35	**5f**	Cl	H	4-$C_2H_5(C_6H_4)$	68/62
3g	Cl	H	3,4-$(CH_3)_2(C_6H_3)$	37	**5g**	Cl	H	3,4-$(CH_3)_2(C_6H_3)$	70/85
3h	Cl	H	2,4-$(CH_3)_2(C_6H_3)$	38	**5h**	Cl	H	2,4-$(CH_3)_2(C_6H_3)$	na/33
3i	Cl	H	2,5-$(CH_3)_2(C_6H_3)$	47	**5i**	Cl	H	2,5-$(CH_3)_2(C_6H_3)$	na/66
4a	Cl	H	CH_3	65	**6a**	H	H	CH_3	60
4b	Cl	H	C_6H_5	69	**6b**	H	NO_2	CH_3	54
4c	Cl	H	4-$Cl(C_6H_4)$	83	**6c**	H	H	4-$Cl(C_6H_4)$	55
4d	Cl	H	4-$C_2H_5(C_6H_4)$	79	**7a**	H	H	CH_3	63
4e	Cl	H	3,4-$(CH_3)_2(C_6H_3)$	83	**7b**	H	NH_2	CH_3	58
					7c	H	H	4-$Cl(C_6H_4)$	57

[a] Isolated yields.
[b] Yield from aniline **4**.
[c] Yield from nitrophthalazinone **3**.



Scheme 5.

phthalazine **3** yielding substituted dialkylaminophenylphthalazinone **8**. This reaction allows introduction of substituents, which are difficult to adopt through *o*-aminophenol or *o*-nitroaniline route. The conversion easily occurs on boiling of phthalazine **3** in an excess of alicyclic amine with fast formation of dialkylamino substituted phthalazinone **8** with high yields (Table 2).

Several dialkylamino derivatives (**8**) have been hydrogenated yielding the relative aniline **9**. On hydrogenation in THF it was found that dialkylamino aniline **9** is much poorly soluble than the relative chlorine derivative **4**. An adequate yield has been obtained for phthalazinones **9a**,**b** (Scheme 5). Subsequent cyclization in PPA gives rise to BIPHs **10a**,**c** with 75% and 87% yields, respectively.

Dialkylaminophthalazinone **8** has been also directly transformed into BIPHs **10** using iron powder in PPA (Scheme 5, Table 3). Samples **10a** and **10c** obtained by two step and one step procedures have proved to be identical. As would be expected the solubility of derivative **8** in PPA was substantially higher than that of chlorine derivative **4**; thus the synthesis may be performed at lower temperature. This is important as some derivatives for instance those of incorporating pyrrolidine moiety happen to be extremely sensitive even to a small rise of temperature and decompose yielding unidentified UV-luminescent products soluble only in acidic water.

Further investigations have shown that PPA may be easily substituted with commercial 85% phosphoric acid. Its boiling point is high enough which makes this solvent advantageous in comparison with aqueous hydrochloric acid. Also above mentioned pyrrolidine derivatives are more stable in reaction conditions and less inclined to the thermal decomposition. Due to rather high water concentration in such an acid some phthalazinones especially those of chlorine substituted **3** could not be dissolved completely. In these cases temperature of the reaction mixture has been enhanced to relative melting point level, this temperature being much lower than that of pure substances and reduction process has been carried out in two-phase medium. This results in an enhancement of duration of synthesis and in consumption of iron powder but practically doesn't influence the yields.

Table 2

R	Nucleophile			
	Morpholine (%)	Pyrrolidine (%)	Piperidine (%)	Piperazine (%)
CH_3	**8a** (71[a])	**8b** (79)	**8c** (74)	**8d** (72)
C_6H_5	**8e** (68)	**8f** (78)	**8g** (81)	
4-$CH_3(C_6H_4)$	**8h** (56)	**8i** (82)	**8j** (76)	
4-$Cl(C_6H_4)$	**8k** (77)	**8l** (87)	**8m** (85)	**8n** (86)
4-$C_2H_5(C_6H_4)$			**8o** (63)	
3,4-$(CH_3)_2(C_6H_3)$			**8p** (80)	
2,5-$(CH_3)_2(C_6H_3)$			**8q** (66)	

[a] Isolated yields.

Table 3

R	9-Substituent			
	Morpholine (%)	Pyrrolidine (%)	Piperidine (%)	Piperazine (%)
CH_3	**10a** (69[a])	**10b** (59)	**10c** (45)	**10d** (81)
C_6H_5	**10e** (56)	**10f** (46)	**10g** (58)	
4-$CH_3(C_6H_4)$	**10h** (50)	**10i** (73)	**10j** (58)	
4-$Cl(C_6H_4)$	**10k** (85)	**10l** (73)	**10m** (64)	**10n** (63)
4-$C_2H_5(C_6H_4)$			**10o** (66)	
3,4-$(CH_3)_2(C_6H_3)$			**10p** (66)	
2,5-$(CH_3)_2(C_6H_3)$			**10q** (57)	

[a] Isolated yields.

3. Conclusion

Thus we have elaborated three-stage procedure of synthesis of substituted benzo[4,5]imidazo[2,1-*a*]phthalazines. Substituents in 5 and 9 positions may be varied in a wide range and amino group may be introduced in 10 position. Nucleophilic substitution of chlorine atom with secondary alicyclic amines in the side benzene ring of phthalazine **3** makes it possible to generate dialkylaminophthalazinone **8** formerly unknown. The latter may be transformed into benzo[4,5]imidazo[2,1-*a*]phthalazine **10** using one-stage or two-stage procedures. The most common use of this method making it possible to vary substituents in **5** and **9** positions has been demonstrated. All the steps of BIPH synthesis are reliable, with high yields and have simple laboratory implementation.

4. Experimental

4.1. General

Melting points were measured on Boetius apparatus and are uncorrected. Infra-red spectra were recorded in KBr tablets on Shimadzu FTIR 8400S instrument. MS spectra were taken on Kratos MS 890. NMR ^{1}H spectra were obtained at 400 MHz and ^{13}C at 100 MHz in $CDCl_3$ or DMSO-d_6 solution on Bruker WM 400 spectrometer. Numeration of locations in phthalazines **3**, **4**, **6**, **8**, and **9** is given in accordance with their appearance in BIPH **5**, **7**, and **10**, as shown in Figure 1.

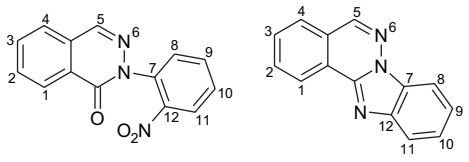


Figure 1. Numeration of locations in phthalazinones and BIPHs.

4.2. Synthesis of nitrophthalazinones 3 and 6 by cyclization of *o*-acylbenzoic acid 2

General method. 2-Acylbenzoic acid (0.060 mol) and appropriate hydrazine (0.057 mol) were refluxed in ethanol–sulfuric acid mixture (80–40 ml) for a given time. The mixture was poured on 300 g of crushed ice and the product precipitated was filtered off. The residue was treated with 5% aqueous NaOH, filtered off, washed with water to neutral pH, and recrystallized from an appropriate solvent.

4.2.1. 2-(2-Nitro-5-chlorophenyl)-1,2-dihydro-1-phthalazinone 3a. Mixture of 2-formylbenzoic acid **2a** (9.0 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1 h. On recrystallization from chloroform–ethanol 7.7 g (45%) of phthalazinone **3a** were obtained as pale yellow crystals, mp 175–177 °C. ν_{max} (KBr): 1663, 1595, 1525, 1343, 752 cm^{-1}. δ_H (DMSO): 8.58 (1H, s, H^5), 8.31 (1H, d, J=7.6 Hz, H^1), 8.16 (1H, d, J=8.8 Hz, H^{11}), 8.05–7.97 (2H, m, H$^{3,\ 4}$), 7.91 (1H, m, H^2), 7.84 (1H, d, J=2.1 Hz, H^8), 7.75 (1H, dd, J=8.8 and 2.1 Hz, H^{10}). δ_C (DMSO): 158.04, 143.43, 139.87, 138.29, 135.43, 134.17, 132.40, 129.31, 129.23, 129.11, 127.16, 126.73, 126.20. Found, %: C 55.59, H 2.53, N 14.15. $C_{14}H_8ClN_3O_3$ (301.69). Requires, %: C 55.74, H 2.67, N 13.93.

4.2.2. 4-Methyl-2-(2-nitro-5-chlorophenyl)-1,2-dihydro-1-phthalazinone 3b. Mixture of 2-acetylbenzoic acid **2b** (9.8 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1 h. After recrystallization from chloroform–ethanol 12.6 g (70%) of phthalazinone **3b** were obtained as pale yellow crystals, mp 168–170 °C. ν_{max} (KBr): 1670, 1604, 1527, 1350, 1334, 1326, 1172, 1142, 773, 753, 690 cm^{-1}. δ_H ($CDCl_3$): 8.48 (1H, d, J=7.8 Hz, H^1), 8.04 (1H, d, J=8.6 Hz, H^{11}), 7.94–7.78 (3H, m, H$^{2,\ 3,\ 4}$), 7.70 (1H, s, H^8), 7.52 (1H, d, J=8.6 Hz, H^{10}), 2.64 (3H, s, CH_3). δ_C (DMSO): 157.87, 145.25, 143.34, 138.14, 135.39, 133.95, 131.97, 129.16, 128.82, 126.55, 125.98, 125.66, 18.29. Found, %: C 57.10, H 3.12, N 13.49. $C_{15}H_{10}ClN_3O_3$ (315.72). Requires, %: C 57.07, H 3.19, N 13.31.

4.2.3. 2-(2-Nitro-5-chlorophenyl)-4-phenyl-1,2-dihydro-1-phthalazinone 3c. Mixture of 2-benzoylbenzoic acid **2c** (13.6 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1 h. After recrystallization from chloroform–ethanol 12.4 g (58%) of phthalazinone **3c** were obtained as pale yellow crystals, mp 137–139 °C. ν_{max} (KBr): 1672, 1599, 1587, 1536, 1472, 1348, 1326, 1137, 739, 692 cm^{-1}. δ_H (DMSO): 8.42 (1H, m, H^1), 8.19 (1H, d, J=8.8 Hz, H^{11}), 8.04–7.92 (3H, m, H$^{3,\ 4,\ 8}$), 7.84–7.75 (2H, m, H$^{4,\ 10}$), 7.69–7.53 (5H, m, C_6H_5). δ_C (DMSO): 157.66, 147.95, 143.40, 138.24, 135.38, 133.97, 133.85, 132.13, 129.26, 129.07, 128.48, 128.23, 127.17, 126.91, 126.12. Found, %: C 63.51, H 3.23, N 11.35. $C_{20}H_{12}ClN_3O_3$ (377.79). Requires, %: C 63.59, H 3.20, N 11.12.

4.2.4. 4-(4-Methylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydro-1-phthalazinone 3d. Mixture of 2-(4-methylbenzoyl)benzoic acid **2d** (14.4 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1 h. After recrystallization from chloroform–ethanol 13.4 g (60%) of phthalazinone **3d** were obtained as pale yellow crystals, mp 184–186 °C. δ_H (DMSO): 8.42 (1H, m, H^1), 8.17 (1H, d, J=8.7 Hz, H^{11}), 7.97 (1H, d, J=1.9 Hz, H^8), 8.01–7.90 (2H, m, H$^{2,\ 3}$), 7.81 (1H, m, H^4), 7.77 (1H, dd, J=8.7 and 1.9 Hz, H^{10}), 7.52 (2H, d, J=7.9 Hz, CH–C(Ar)–CH), 7.36 (2H, d, J=7.9 Hz, CH–C(Me)–CH), 2.43 (3H, s, CH_3). δ_C (DMSO): 157.64, 147.97, 143.35, 138.78, 138.22, 135.37, 133.92, 132.03, 131.02, 129.20, 128.95, 128.82, 128.56, 127.15, 126.91, 126.05, 20.71. Found, %: C 64.24, H 3.48, N 10.92. $C_{21}H_{14}ClN_3O_3$ (391.82). Requires, %: C 64.38, H 3.60, N 10.72.

4.2.5. 2-(2-Nitro-5-chlorophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 3e. Mixture of 2-(4-chlorobenzoyl)benzoic acid **2e** (15.6 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1 h. After recrystallization from chloroform–ethanol 12.4 g (53%) phthalazinone **3e** were obtained as pale yellow crystals, mp 190–192 °C. δ_H (DMSO): 8.42 (1H, m, H^1), 8.18 (1H, d, J=8.8 Hz, H^{11}), 8.04–7.94 (3H, m, H$^{2,\ 3,\ 8}$), 7.83–7.75 (2H, m, H$^{4,\ 10}$), 7.69 (2H, d, J=7.9 Hz, CH–C(Cl)–CH), 7.61 (2H, d, J=7.9 Hz, CH–C(Ar)–CH). δ_C (DMSO): 157.62, 146.87, 143.31, 138.32, 135.24, 134.55, 134.06, 132.56, 132.19, 130.79, 129.23, 129.07, 128.44, 128.25, 127.11, 126.97, 126.64, 126.06. Found, %: C 58.24, H 2.70, N 10.40. $C_{20}H_{11}Cl_2N_3O_3$ (412.23). Requires, %: C 58.27, H 2.69, N 10.19.

4.2.6. 2-(2-Nitro-5-chlorophenyl)-4-(4-ethylphenyl)-1,2-dihydro-1-phthalazinone 3f. Mixture of 2-(4-ethylbenzoyl)benzoic acid **2f** (15.2 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1.5 h. After recrystallization from chloroform–ethanol 8.1 g (35%) of phthalazinone **3f** were obtained as pale yellow crystals, mp 218–220 °C. δ_H (DMSO): 8.41 (1H, m, H^1), 8.21 (1H, d, J=8.6 Hz, H^{11}), 8.11–7.96 (3H, m, H$^{2,\ 3,\ 8}$), 7.88–7.79 (2H, m, H$^{4,\ 10}$), 7.57 (2H, d, J=7.4 Hz, CH–C(Ar)–CH), 7.42 (2H, d, J=7.4 Hz, CH–C(Alk)–CH), 2.69 (2H, q, J=7.4 Hz, CH_2), 1.24 (3H, t, J=7.4 Hz, CH_3). Found, %: C 65.00, H 3.87, N 10.57. $C_{22}H_{16}ClN_3O_3$ (405.84). Requires, %: C 65.11, H 3.97, N 10.35.

4.2.7. 4-(3,4-Dimethylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydro-1-phthalazinone 3g. Mixture of 2-(3,4-dimethylbenzoyl)benzoic acid **2g** (15.2 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1.5 h. After recrystallization from chloroform–ethanol 8.6 g (37%) of phthalazinone **3g** were obtained as pale yellow crystals, mp 238–240 °C. δ_H (DMSO): 8.39 (1H, m, H^1), 8.20 (1H, d, J=8.8 Hz, H^{11}), 8.10–7.94 (3H, m, $H^{2,\ 3,\ 8}$), 7.87–7.78 (2H, m, $H^{4,\ 10}$), 7.44–7.30 (3H, m, $(CH_3)_2$–C_6H_3), 2.31 (6H, s, $2CH_3$). Found, %: C 64.97, H 3.81, N 10.56. $C_{22}H_{16}ClN_3O_3$ (405.84). Requires, %: C 65.11, H 3.97, N 10.35.

4.2.8. 4-(2,4-Dimethylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydro-1-phthalazinone 3h. Mixture of 2-(2,4-dimethylbenzoyl)benzoic acid **2h** (15.2 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1.5 h. After recrystallization from chloroform–ethanol 8.8 g (38%) of phthalazinone **3h** were obtained as pale yellow crystals, mp 204–206 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.21 (1H, d, J=8.8 Hz, H^{11}), 8.04 (1H, d, J=2.0 Hz, H^8), 8.01–7.92 (2H, m, $H^{2,\ 3}$), 7.83 (1H, dd, J=8.8 and 2.0 Hz, H^{10}), 7.32 (1H, m, H^4), 7.25–7.14 (3H, m, $(CH_3)_2$–C_6H_3), 2.37 (3H, s, 2′-CH_3), 2.09 (3H, s, 4′-CH_3). δ_C (DMSO): 157.79, 148.28, 143.48, 138.46, 138.14, 136.13, 135.50, 134.04, 132.14, 130.72, 130.37, 129.40, 129.29, 129.14, 126.97, 126.71, 126.18, 20.66, 18.96. Found, %: C 65.10, H 3.89, N 10.52. $C_{22}H_{16}ClN_3O_3$ (405.84). Requires, %: C 65.11, H 3.97, N 10.35.

4.2.9. 4-(2,5-Dimethylphenyl)-2-(2-nitro-5-chlorophenyl)-1,2-dihydro-1-phthalazinone 3i. Mixture of 2-(2,5-dimethylbenzoyl)benzoic acid **2i** (15.2 g) and 2-nitro-5-chlorophenylhydrazine **1a** (10.7 g) was refluxed for 1.5 h. After recrystallization from chloroform–ethanol 10.9 g (47%) of phthalazinone **3i** were obtained as pale yellow crystals, mp 205–207 °C. δ_H (DMSO): 8.42 (1H, m, H^1), 8.15 (1H, d, J=8.9 Hz, H^{11}), 7.93–7.86 (2H, m, $H^{2,\ 3}$), 7.83 (1H, d, J=2.2 Hz, H^8), 7.77 (1H, dd, J=8.9 and 2.2 Hz, H^{10}), 7.37 (1H, m, H^4), 7.24–7.12 (3H, m, $(CH_3)_2$–C_6H_3), 2.38 (3H, s, 2′-CH_3), 2.13 (3H, s, 5′-CH_3). Found, %: C 65.07, H 3.91, N 10.54. $C_{22}H_{16}ClN_3O_3$ (405.84). Requires, %: C 65.11, H 3.97, N 10.35.

4.2.10. 4-Methyl-2-(2-nitrophenyl)-1,2-dihydro-1-phthalazinone 6a. 2-Acetylbenzoic acid **2b** (9.8 g) and 2-nitrophenylhydrazine **1b** (8.8 g) in the mixture of 40 ml of ethanol and 40 ml of sulfuric acid were refluxed for 1.5 h. After recrystallization from chloroform–ethanol 9.6 g (60%) of phthalazinone **6a** were obtained as pale yellow crystals, mp 195–197 °C (lit. mp 203–204 °C[8]). ν_{max} (KBr): 1668, 1533, 1356, 1340, 1175, 777, 687 cm^{-1}. δ_H (DMSO): 8.32 (1H, d, J=7.5 Hz, H^1), 8.10 (1H, d, J=7.9 Hz, H^{11}), 8.02–7.62 (6H, m, $H^{2,\ 3,\ 4,\ 8,\ 9,\ 10}$), 2.62 (3H, s, CH_3). δ_C (DMSO): 157.95, 144.81, 144.74, 134.25, 133.74, 131.84, 129.33, 129.19, 128.88, 126.58, 126.47, 125.53, 124.18, 18.35. Found, %: C 63.81, H 3.82, N 15.14. $C_{15}H_{11}N_3O_3$ (281.27). Requires, %: C 64.05, H 3.94, N 14.94.

4.2.11. 2-(2,4-Dinitrophenyl)-4-methyl-1,2-dihydro-1-phthalazinone 6b. 2-Acetylbenzoic acid **2b** (9.9 g) and 2,4-dinitrophenylhydrazine **1c** (11.4 g) in the mixture of 40 ml of ethanol and 40 ml of sulfuric acid were refluxed for 1.5 h. After recrystallization from DMF 9.9 g (54%) of phthalazinone **6b** were obtained as pale yellow crystals, mp 244–246 °C (lit. mp 248[9]). ν_{max} (KBr): 3073, 1671, 1608, 1540, 1530, 1350, 1337, 773 cm^{-1}. δ_H (DMSO): 8.81 (1H, d, J=1.8 Hz, H^{11}), 8.72 (1H, dd, J=8.9 and 1.8 Hz, H^9), 8.36 (1H, d, J=7.5 Hz, H^1), 8.09 (1H, d, J=8.9 Hz, H^8), 8.06–8.00 (2H, m, $H^{3,\ 4}$), 7.94 (1H, m, H^2), 2.66 (3H, s, CH_3). δ_C (DMSO): 158.09, 146.43, 146.11, 144.29, 138.47, 134.65, 132.65, 130.84, 129.20, 128.38, 126.63, 126.25, 126.25, 120.19, 18.50. Found, %: C 55.05, H 3.00, N 17.34. $C_{15}H_{10}N_4O_5$ (326.27). Requires, %: C 55.22, H 3.09, N 17.17.

4.2.12. 2-(2-Nitrophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 6c. 2-(4-Chlorobenzoyl)benzoic acid **2e** (15.6 g) and 2-nitrophenylhydrazine **1b** (8.7 g) in the mixture of 40 ml of ethanol and 40 ml of sulfuric acid were refluxed for 1 h. After recrystallization from ethanol 6.0 g (55%) of phthalazinone **6c** were obtained as pale yellow crystals, mp 167–169 °C. δ_H (DMSO): 8.43 (1H, m, H^1), 8.09 (1H, dd, J=8.0 and 1.2 Hz, H^{11}), 7.76 (10H, m, $H^{2,\ 3,\ 4,\ 8,\ 9,\ 10}$, p-Cl–C_6H_4). δ_C (DMSO): 157.72, 146.54, 144.77, 134.51, 134.17, 134.00, 133.82, 132.78, 132.19, 130.87, 129.44, 129.17, 128.47, 128.32, 127.33, 127.05, 126.62, 124.37. Found, %: C 63.41, H 3.29, N 11.33. $C_{20}H_{12}ClN_3O_3$ (377.79). Requires, %: C 63.59, H 3.20, N 11.12.

4.3. Synthesis of nitrophthalazinone 8 by nucleophilic substitution in 2-(2-nitro-5-chlorophenyl)phthalazinone 3

General method. A solution of phthalazinone **3** (0.010 mol) in 10 ml of alicyclic amine was refluxing for 1.5 h. Reaction mixture was poured in 100 ml of hot water. The residual oil, which solidified upon cooling, was grinded and filtered off. On washing with hot water the residue was dried and recrystallized from an appropriate solvent.

4.3.1. 4-Methyl-2-(2-nitro-5-morpholinophenyl)-1,2-dihydro-1-phthalazinone 8a. From phthalazinone **3b** (3.16 g) and morpholine after recrystallization from chloroform–methanol 2.63 g (71%) of product **8a** were obtained as yellow crystals, mp 200–202 °C. ν_{max} (KBr): 1653, 1601, 1506, 1317, 1244, 1101 cm^{-1}. δ_H (DMSO): 8.31 (1H, d, J=7.8 Hz, H^1), 8.10 (1H, d, J=10.0 Hz, H^{11}), 8.00–7.95 (2H, m, $H^{3,\ 4}$), 7.90 (1H, m, H^2), 7.12–7.03 (2H, m, $H^{8,\ 10}$), 3.75 (4H, m, CH_2OCH_2), 3.43 (4H, m, CH_2NCH_2), 2.60 (3H, s, CH_3). δ_C (DMSO): 158.08, 154.18, 143.77, 137.43, 134.13, 133.48, 131.50, 129.27, 126.89, 126.28, 125.33, 113.45, 111.87, 65.51, 46.33, 18.27. Found, %: C 62.00, H 4.74, N 15.51. $C_{19}H_{18}N_4O_4$ (366.38). Requires, %: C 62.29, H 4.95, N 15.29.

4.3.2. 4-Methyl-2-(2-nitro-5-pyrrolidinophenyl)-1,2-dihydro-1-phthalazinone 8b. From phthalazinone **3b** (3.16 g) and pyrrolidine after recrystallization from chloroform–methanol 2.81 g (79%) of product **8b** were obtained as yellow crystals, mp 235–237 °C. δ_H ($CDCl_3$): 8.51 (1H, d, J=7.2 Hz, H^1), 8.22 (1H, d, J=10.0 Hz, H^{11}), 7.91–7.74 (3H, m, $H^{2,\ 3,\ 4}$), 6.59–6.51 (2H, m, $H^{8,\ 10}$), 3.42 (4H, m, CH_2NCH_2), 2.62 (3H, s, CH_3), 2.06 (4H, m, CH_2CH_2). δ_C

(DMSO): 158.09, 151.25, 143.56, 137.93, 133.46, 131.95, 131.54, 129.34, 127.34, 127.03, 126.23, 125.41, 111.70, 110.23, 47.55, 24.73, 18.33. Found, %: C 64.89, H 5.11, N 16.18. $C_{19}H_{18}N_4O_3$ (350.38). Requires, %: C 65.13, H 5.18, N 15.99.

4.3.3. 4-Methyl-2-(2-nitro-5-piperidinophenyl)-1,2-dihydro-1-phthalazinone 8c. From phthalazinone **3b** (3.16 g) and piperidine after recrystallization from chloroform–methanol 2.70 g (74%) of product **8c** were obtained as yellow crystals, mp 202–204 °C. δ_H ($CDCl_3$): 8.50 (1H, d, J=7.3 Hz, H^1), 8.16 (1H, d, J=10.0 Hz, H^{11}), 7.92–7.74 (3H, m, $H^{2,\ 3,\ 4}$), 6.88–6.79 (2H, m, $H^{8,\ 10}$), 3.43 (4H, m, CH_2NCH_2), 2.62 (3H, s, CH_3), 1.67 (6H, m, $CH_2CH_2CH_2$). Found, %: C 65.77, H 5.32, N 15.60. $C_{20}H_{20}N_4O_3$ (364.41). Requires, %: C 65.92, H 5.53, N 15.37.

4.3.4. 4-Methyl-2-(2-nitro-5-piperazinophenyl)-1,2-dihydro-1-phthalazinone 8d. From phthalazinone **3b** (3.16 g) and piperazine after recrystallization from chloroform–ethanol 2.63 g (72%) of the product **8d** were obtained as yellow crystals, mp 187–189 °C. δ_H (DMSO): 8.31 (1H, d, J=7.5 Hz, H^1), 8.08 (1H, d, J=9.0 Hz, H^{11}), 8.00–7.93 (2H, m, $H^{3,\ 4}$), 7.88 (1H, m, H^2), 7.08–6.97 (2H, m, $H^{8,\ 10}$), 3.39 (4H, m, CH_2–N(Ar)–CH_2), 2.85 (4H, m, C*H*$_2$–NH–C*H*$_2$), 2.59 (3H, s, CH_3). Found, %: C 62.40, H 5.14, N 19.39. $C_{19}H_{19}N_5O_3$ (365.39). Requires, %: C 62.46, H 5.24, N 19.17.

4.3.5. 2-(2-Nitro-5-morpholinophenyl)-4-phenyl-1,2-dihydro-1-phthalazinone 8e. From phthalazinone **3c** (3.78 g) and morpholine after recrystallization from chloroform–methanol 2.91 g (68%) of product **8e** were obtained as yellow crystals, mp 240–242 °C. ν_{max} (KBr): 1653, 1601, 1582, 1491, 1325, 1244 cm^{-1}. δ_H (DMSO): 8.41 (1H, m, H^1), 8.13 (1H, d, J=9.2 Hz, H^{11}), 8.02–7.89 (2H, m, $H^{2,\ 3}$), 7.80 (1H, m, H^4), 7.67–7.50 (5H, m, C_6H_5), 7.19 (1H, d, J=2.1 Hz, H^8), 7.10 (1H, dd, J=9.2 and 2.1 Hz, H^{10}), 3.74 (4H, m, CH_2OCH_2), 3.43 (4H, m, CH_2NCH_2). δ_C (DMSO): 157.78, 154.23, 146.65, 137.38, 134.23, 134.09, 133.52, 131.68, 129.12, 128.89, 128.56, 128.18, 127.59, 126.99, 126.67, 126.54, 113.44, 112.08, 65.53, 46.35. Found, %: C 67.09, H 4.66, N 13.30. $C_{24}H_{20}N_4O_4$ (428.45). Requires, %: C 67.28, H 4.71, N 13.08.

4.3.6. 2-(2-Nitro-5-pyrrolidinophenyl)-4-phenyl-1,2-dihydro-1-phthalazinone 8f. From phthalazinone **3c** (3.78 g) and pyrrolidine after recrystallization from chloroform–ethanol 3.25 g (78%) of product **8f** were obtained as yellow crystals, mp 211–213 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.14 (1H, d, J=9.2 Hz, H^{11}), 8.04–7.91 (2H, m, $H^{2,\ 3}$), 7.80 (1H, m, H^4), 7.67–7.51 (5H, m, C_6H_5), 6.83 (1H, s, H^8), 6.71 (1H, d, J=9.2 Hz, H^{10}), 3.40 (4H, m, CH_2NCH_2), 1.98 (4H, m, CH_2CH_2). δ_C (DMSO): 157.86, 151.23, 146.47, 137.83, 134.28, 133.51, 131.88, 131.67, 129.12, 128.90, 128.57, 128.20, 127.65, 127.43, 126.62, 126.48, 111.71, 110.37, 47.59, 24.75. Found, %: C 69.67, H 4.75, N 13.73. $C_{24}H_{20}N_4O_3$ (412.45). Requires, %: C 69.89, H 4.89, N 13.58.

4.3.7. 2-(2-Nitro-5-piperidinophenyl)-4-phenyl-1,2-dihydro-1-phthalazinone 8g. From phthalazinone **3c** (3.78 g) and piperidine after recrystallization from chloroform–ethanol 3.45 g (81%) of product **8g** were obtained as yellow crystals, mp 235–237 °C. δ_H (DMSO): 8.41 (1H, m, H^1), 8.09 (1H, d, J=9.5 Hz, H^{11}), 8.01–7.89 (2H, m, $H^{2,\ 3}$), 7.79 (1H, m, H^4), 7.67–7.51 (5H, m, C_6H_5), 7.11 (1H, d, J=2.4 Hz, H^8), 7.02 (1H, dd, J=9.5 and 2.4 Hz, H^{10}), 3.49 (4H, s, CH_2NCH_2), 1.63 (6H, s, $CH_2CH_2CH_2$). Found, %: C 70.29, H 4.96, N 13.32. $C_{25}H_{22}N_4O_3$ (426.48). Requires, %: C 70.41, H 5.20, N 13.14.

4.3.8. 4-(4-Methylphenyl)-2-(2-nitro-5-morpholinophenyl)-1,2-dihydro-1-phthalazinone 8h. From phthalazinone **3d** (3.92 g) and morpholine after recrystallization from chloroform–methanol 2.48 g (56%) of product **8h** were obtained as yellow crystals, mp 240–242 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.12 (1H, d, J=9.2 Hz, H^{11}), 7.98–7.87 (2H, m, $H^{2,\ 3}$), 7.81 (1H, m, H^4), 7.35 (2H, d, J=7.7 Hz, CH–C(Alk)–CH), 7.32 (2H, d, J=7.7 Hz, CH–C(Ar)–CH), 7.15 (1H, d, J=2.1 Hz, H^8), 7.08 (1H, dd, J=9.2 and 2.1 Hz, H^{10}), 3.73 (4H, m, CH_2OCH_2), 3.41 (4H, m, CH_2NCH_2), 2.42 (3H, s, CH_3). Found, %: C 67.62, H 4.75, N 12.85. $C_{25}H_{22}N_4O_4$ (442.48). Requires, %: C 67.86, H 5.01, N 12.66.

4.3.9. 4-(4-Methylphenyl)-2-(2-nitro-5-pyrrolidinophenyl)-1,2-dihydro-1-phthalazinone 8i. From phthalazinone **3d** (3.92 g) and pyrrolidine after recrystallization from chloroform–ethanol 3.49 g (82%) of product **8i** were obtained as yellow crystals, mp>260 °C. δ_H (DMSO): 8.39 (1H, m, H^1), 8.12 (1H, d, J=8.8 Hz, H^{11}), 7.99–7.87 (2H, m, $H^{2,\ 3}$), 7.82 (1H, m, H^4), 7.50 (2H, d, J=7.2 Hz, CH–C(Ar)–CH), 7.35 (2H, d, J=7.2 Hz, CH–C(Alk)–CH), 6.75–6.62 (2H, m, $H^{8,\ 10}$), 3.41 (4H, s, CH_2NCH_2), 2.42 (3H, s, CH_3), 2.02 (4H, s, CH_2CH_2). Found, %: C 70.31, H 5.17, N 13.29. $C_{25}H_{22}N_4O_3$ (426.48). Requires, %: C 70.41, H 5.20, N 13.14.

4.3.10. 4-(4-Methylphenyl)-2-(2-nitro-5-piperidinophenyl)-1,2-dihydro-1-phthalazinone 8j. From phthalazinone **3d** (3.92 g) and piperidine after recrystallization from chloroform–ethanol 3.34 g (76%) of product **8j** were obtained as yellow crystals, mp 161–163 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.09 (1H, d, J=9.3 Hz, H^{11}), 7.99–7.88 (2H, m, $H^{2,\ 3}$), 7.81 (1H, m, H^4), 7.51 (2H, d, J=7.6 Hz, CH–C(Ar)–CH), 7.35 (2H, d, J=7.6 Hz, CH–C(Alk)–CH), 7.11 (1H, d, J=2.3 Hz, H^8), 7.04 (1H, dd, J=9.3 and 2.3 Hz, H^{10}), 3.49 (4H, s, CH_2NCH_2), 2.42 (3H, s, CH_3), 1.63 (6H, s, $CH_2CH_2CH_2$). Found, %: C 70.78, H 5.25, N 12.93. $C_{26}H_{24}N_4O_3$ (440.51). Requires, %: C 70.89, H 5.49, N 12.72.

4.3.11. 2-(2-Nitro-5-morpholinophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 8k. From phthalazinone **3e** (4.12 g) and morpholine after recrystallization from chloroform–methanol 3.57 g (77%) of product **8k** were *obtained* as yellow crystals, mp 230–232 °C. δ_H (DMSO): 8.41 (1H, m, H^1), 8.13 (1H, d, J=9.3 Hz, H^{11}), 8.02–7.90 (2H, m, $H^{2,\ 3}$), 7.79 (1H, m, H^4), 7.67 (2H, d, J=8.7 Hz, CH–C(Cl)–CH), 7.59 (2H, d, J=8.7 Hz, CH–C(Ar)–CH), 7.19 (1H, d, J=2.1 Hz, H^8), 7.09 (1H, dd, J=9.3 and 2.1 Hz, H^{10}), 3.74 (4H, m, CH_2OCH_2), 3.43 (4H, m, CH_2NCH_2). δ_C (DMSO): 157.83, 154.29, 145.65, 137.32, 134.35, 134.04, 133.70, 132.94, 131.90, 130.95, 128.44, 127.56, 127.07, 126.85, 126.40, 113.45, 112.11, 65.57, 46.35. Found, %: C 62.19, H 4.25, N 12.31. $C_{24}H_{19}ClN_4O_4$ (462.90). Requires, %: C 62.27, H 4.14, N 12.10.

4.3.12. 2-(2-Nitro-5-pyrrolidinophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 8l. From phthalazinone **3e** (4.12 g) and pyrrolidine after recrystallization from chloroform–ethanol 3.89 g (87%) of product **8l** were obtained as yellow crystals, mp 265–267 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.10 (1H, d, J=9.1 Hz, H^{11}), 8.01–7.89 (2H, m, $H^{2,\ 3}$), 7.78 (1H, m, H^4), 7.66 (2H, d, J=8.5 Hz, CH–C(Cl)–CH), 7.58 (2H, d, J=8.5 Hz, CH–C(Ar)–CH), 6.74 (1H, d, J=2.5 Hz, H^8), 6.70 (1H, dd, J=9.1 and 2.5 Hz, H^{10}), 3.39 (4H, m, CH_2NCH_2), 2.00 (4H, m, CH_2CH_2). δ_C (DMSO): 157.83, 151.30, 145.40, 137.75, 134.24, 133.69, 133.07, 131.88, 130.97, 128.42, 127.67, 127.53, 126.82, 126.37, 111.68, 110.50, 47.70, 24.84. Found, %: C 64.56, H 4.27, N 12.73. $C_{24}H_{19}ClN_4O_3$ (446.90). Requires, %: C 64.50, H 4.29, N 12.54.

4.3.13. 2-(2-Nitro-5-piperidinophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 8m. From phthalazinone **3e** (4.12 g) and piperidine after recrystallization from chloroform–methanol 3.92 g (85%) of product **8m** were obtained as yellow crystals, mp 221–223 °C. δ_H (DMSO): 8.41 (1H, m, H^1), 8.08 (1H, d, J=9.2 Hz, H^{11}), 8.01–7.88 (2H, m, $H^{2,\ 3}$), 7.78 (1H, m, H^4), 7.66 (2H, d, J=8.5 Hz, CH–C(Cl)–CH), 7.58 (2H, d, J=8.5 Hz, CH–C(Ar)–CH), 7.10 (1H, d, J=2.2 Hz, H^8), 7.03 (1H, dd, J=9.2 and 2.2 Hz, H^{10}), 3.49 (4H, s, CH_2NCH_2), 1.62 (6H, s, $CH_2CH_2CH_2$). Found, %: C 65.08, H 4.61, N 12.35. $C_{25}H_{21}ClN_4O_3$ (460.92). Requires, %: C 65.15, H 4.59, N 12.16.

4.3.14. 2-(2-Nitro-5-piperazinophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 8n. From phthalazinone **3e** (4.12 g) and piperazine after recrystallization from chloroform–ethanol 3.97 g (86%) of product **8n** were obtained as yellow crystals, mp 225–227 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.11 (1H, d, J=9.4 Hz, H^{11}), 7.96 (2H, m, $H^{2,\ 3}$), 7.78 (1H, m, H^4), 7.65 (4H, m, p-Cl–C_6H_4), 7.14 (1H, d, J=2.2 Hz, H^8), 7.06 (1H, dd, J=9.4 and 2.2 Hz, H^{10}), 3.41 (4H, m, CH_2–N(Ar)–CH_2), 3.34 (1H, s, NH), 2.85 (4H, m, CH_2–NH–CH_2). Found, %: C 62.46, H 4.47, N 15.35. $C_{24}H_{20}ClN_5O_3$ (461.91). Requires, %: C 62.41, H 4.36, N 15.16.

4.3.15. 2-(2-Nitro-5-piperidinophenyl)-4-(4-ethylphenyl)-1,2-dihydro-1-phthalazinone 8o. From phthalazinone **3f** (4.06 g) and piperidine after recrystallization from chloroform–methanol 2.87 g (63%) of product **8o** were obtained as yellow crystals, mp 222–224 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.08 (1H, d, J=10.2 Hz, H^{11}), 7.97–7.87 (2H, m, $H^{2,\ 3}$), 7.83 (1H, m, H^4), 7.53 (2H, d, J=7.8 Hz, CH–C(Ar)–CH), 7.36 (2H, d, J=7.8 Hz, CH–C(Alk)–CH), 7.07–6.98 (2H, m, $H^{8,\ 10}$), 3.50 (4H, s, CH_2NCH_2), 2.73 (2H, q, J=7.6 Hz, CH_2), 1.66 (6H, s, $CH_2CH_2CH_2$), 1.29 (3H, t, J=7.6 Hz, CH_3). Found, %: C 71.13, H 5.59, N 12.51. $C_{27}H_{26}N_4O_3$ (454.53). Requires, %: C 71.35, H 5.77, N 12.33.

4.3.16. 4-(3,4-Dimethylphenyl)-2-(2-nitro-5-piperidinophenyl)-1,2-dihydro-1-phthalazinone 8p. From phthalazinone **3g** (4.06 g) and piperidine after recrystallization from chloroform–methanol 3.64 g (80%) of product **8p** were obtained as yellow crystals, mp 238–240 °C. δ_H (DMSO): 8.39 (1H, m, H^1), 8.10 (1H, d, J=8.9 Hz, H^{11}), 7.97–7.78 (3H, m, $H^{2,\ 3,\ 4}$), 7.41–7.23 (3H, m, $(CH_3)_2$–C_6H_3), 7.08–6.95 (2H, m, $H^{8,\ 10}$), 3.50 (4H, s, CH_2NCH_2), 2.34 (6H, s, $2CH_3$), 1.67 (6H, s, $CH_2CH_2CH_2$). Found, %: C 71.25, H 5.61, N 12.55. $C_{27}H_{26}N_4O_3$ (454.53). Requires, %: C 71.35, H 5.77, N 12.33.

4.3.17. 4-(2,5-Dimethylphenyl)-2-(2-nitro-5-piperidinophenyl)-1,2-dihydro-1-phthalazinone 8q. From phthalazinone **3i** (4.06 g) and piperidine after recrystallization from chloroform–methanol 3.00 g (66%) of product **8q** were obtained as yellow crystals, mp 205–207 °C. δ_H (DMSO): 8.41 (1H, m, H^1), 8.09 (1H, d, J=9.0 Hz, H^{11}), 7.93–7.80 (2H, m, $H^{2,\ 3}$), 7.35 (1H, m, H^4), 7.25–7.12 (3H, m, $(CH_3)_2$–C_6H_3), 7.05–6.95 (2H, m, $H^{8,\ 10}$), 3.49 (4H, s, CH_2NCH_2), 2.37 (3H, s, 2′-CH_3), 2.13 (3H, s, 5′-CH_3), 1.67 (6H, s, $CH_2CH_2CH_2$). Found, %: C 71.02, H 5.76, N 12.53. $C_{27}H_{26}N_4O_3$ (454.53). Requires, %: C 71.35, H 5.77, N 12.33.

4.4. Aminophthalazinones 4 and 9

General method for nitro group catalytic reduction. Solution of 0.004 mol of nitrophthalazinone in 40 ml of THF was hydrogenated over 100 mg of 5% palladium charcoal with shaking at room temperature and atmospheric pressure. On absorption of the calculated volume of hydrogen the catalyst powder was filtered off and the solution was concentrated under reduced pressure to 10 ml volume. The product was precipitated by dilution with light petroleum ether to total volume of 100 ml. The product was filtered off, washed with petroleum ether, and air-dried. As recrystallization of amines **4**, **9** leads to accumulation of impurities they are described as being isolated from the reaction mixture.

4.4.1. 2-(2-Amino-5-chlorophenyl)-4-methyl-1,2-dihydro-1-phthalazinone 4a. From of nitrophthalazinone **3b** (1.24 g) was obtained 0.74 g (65%) of aminophthalazinone **4a** as greenish-yellow crystals, mp 195–196 °C. ν_{max} (KBr): 3422, 3341, 1656, 1632, 1589, 1499, 1345, 771, 695 cm^{-1}. δ_H ($CDCl_3$): 8.51 (1H, d, J=7.2 Hz, H^1), 7.93–7.75 (3H, m, $H^{2,\ 3,\ 4}$), 7.30 (1H, s, H^8), 7.16 (1H, d, J=8.4 Hz, H^{10}), 6.79 (1H, d, J=8.4 Hz, H^{11}), 3.92 (2H, s, NH_2), 2.63 (3H, s, CH_3). δ_H (DMSO): 157.86, 144.26, 143.04, 133.09, 131.21, 129.37, 128.23, 127.80, 127.75, 127.62, 126.37, 125.14, 118.66, 117.22, 18.39. Found, %: C 63.10, H 4.22, N 14.94. $C_{15}H_{12}ClN_3O$ (285.74). Requires, %: C 63.05, H 4.23, N 14.71.

4.4.2. 2-(2-Amino-5-chlorophenyl)-4-phenyl-1,2-dihydro-1-phthalazinone 4b. From nitrophthalazinone **3c** (1.51 g) was obtained 0.96 g (69%) of aminophthalazinone **4b** as colorless crystal, mp 185–187 °C. ν_{max} (KBr): 3400, 3327, 1647, 1492, 1334, 789, 698 cm^{-1}. δ_H ($CDCl_3$): 8.60 (1H, m, H^1), 7.90–7.77 (3H, m, $H^{2,\ 3,\ 4}$), 7.68–7.48 (5H, m, C_6H_5), 7.39 (1H, d, J=2.3 Hz, H^8), 7.17 (1H, dd, J=8.7 and 2.3 Hz, H^{10}), 6.77 (1H, d, J=8.7 Hz, H^{11}), 3.98 (2H, s, NH_2). δ_H (DMSO): 157.72, 147.24, 143.26, 134.57, 133.00, 131.24, 129.18, 128.81, 128.70, 128.45, 128.07, 127.68, 127.48, 126.67, 126.36, 118.47, 117.15. Found, %: C 69.01, H 4.00, N 12.29. $C_{20}H_{14}ClN_3O$ (347.81). Requires, %: C 69.07, H 4.06, N 12.08.

4.4.3. 2-(2-Amino-5-chlorophenyl)-4-(4-chlorophenyl)-1,2-dihydro-1-phthalazinone 4c. From nitrophthalazinone

3e (1.65 g) was obtained 1.27 g (83%) of aminophthalazinone **4c** as colorless crystal, mp 193–195 °C. δ_H (DMSO): 8.46 (1H, m, H^1), 7.98–7.86 (2H, m, $H^{2,3}$), 7.75 (1H, m, H^4), 7.66 (2H, d, J=8.4 Hz, CH–C(Cl)–CH), 7.54 (2H, d, J=8.4 Hz, CH–C(Ar)–CH), 7.37 (1H, d, J=1.9 Hz, H^8), 7.32 (1H, dd, J=8.7 and 1.9 Hz, H^{10}), 7.18 (1H, d, J=8.7 Hz, H^{11}), 5.74 (2H, s, NH_2). Found, %: C 62.89, H 3.39, N 11.20. $C_{20}H_{13}Cl_2N_3O$ (382.25). Requires, %: C 62.84, H 3.43, N 10.99.

4.4.4. 2-(2-Amino-5-chlorophenyl)-4-(4-ethylphenyl)-1,2-dihydro-1-phthalazinone 4d. From nitrophthalazinone **3f** (1.62 g) was obtained 1.19 g (79%) of aminophthalazinone **4d** as colorless crystal, mp 168–170 °C. δ_H (DMSO): 8.40 (1H, m, H^1), 8.01–7.85 (2H, m, $H^{2,3}$), 7.75 (1H, m, H^4), 7.58–7.34 (4H, m, *p*-Et–C_6H_4), 7.22 (1H, d, J=1.9 Hz, H^8), 7.16 (1H, dd, J=8.7 and 1.9 Hz, H^{10}), 6.84 (1H, d, J=8.7 Hz, H^{11}), 5.36 (2H, s, NH_2), 2.65 (2H, q, J=7.5 Hz, CH_2), 1.23 (3H, t, J=7.5 Hz, CH_3). Found, %: C 70.24, H 4.77, N 11.41. $C_{22}H_{18}ClN_3O$ (375.86). Requires, %: C 70.30, H 4.83, N 11.18.

4.4.5. 2-(2-Amino-5-chlorophenyl)-4-(3,4-dimethylphenyl)-1,2-dihydro-1-phthalazinone 4e. From nitrophthalazinone **3h** (1.62 g) was obtained 1.25 g (83%) of aminophthalazinone **4e** as colorless crystal, mp 190–192 °C. δ_H (DMSO): 8.39 (1H, m, H^1), 8.01–7.85 (2H, m, $H^{2,3}$), 7.75 (1H, m, H^4), 7.39–7.30 (3H, m, $(CH_3)_2$–C_6H_3), 7.22 (1H, d, J=2.1 Hz, H^8), 7.15 (1H, dd, J=8.7 and 2.1 Hz, H^{10}), 6.81 (1H, d, J=8.7 Hz, H^{11}), 5.35 (2H, s, NH_2), 2.31 (6H, s, $2CH_3$). Found, %: C 70.24, H 4.77, N 11.41. $C_{22}H_{18}ClN_3O$ (375.86). Requires, %: C 70.30, H 4.83, N 11.18.

4.4.6. 2-(2-Amino-5-morpholinophenyl)-4-methyl-1,2-dihydro-1-phthalazinone 9a. From nitrophthalazinone **8a** (1.46 g) was obtained 0.96 g (71%) of aminophthalazinone **9a** as colorless crystal, mp 155–157 °C. ν_{max} (KBr): 3395, 3302, 1663, 1508, 1329, 1115, 768 cm^{-1}. δ_H (DMSO): 8.38 (1H, d, J=7.4 Hz, H^1), 7.98–7.90 (2H, m, $H^{3,4}$), 7.86 (1H, m, H^2), 6.91–6.65 (3H, m, $H^{8,10,11}$), 4.29 (2H, s, NH_2), 3.73 (4H, m, CH_2OCH_2), 2.96 (4H, m, CH_2NCH_2), 2.60 (3H, s, CH_3). δ_H (DMSO): 157.80, 143.86, 142.81, 137.31, 133.10, 131.26, 129.32, 128.39, 127.77, 126.45, 125.15, 117.85, 117.35, 116.07, 66.16, 50.28, 18.48. Found, %: C 67.56, H 5.90, N 16.86. $C_{19}H_{20}N_4O_2$ (336.40). Requires, %: C 67.84, H 5.99, N 16.65.

4.4.7. 2-(2-Amino-5-piperidinophenyl)-4-methyl-1,2-dihydro-1-phthalazinone 9b. From nitrophthalazinone **8c** (1.46 g) was obtained 1.06 g (79%) of aminophthalazinone **9b** as colorless crystal, mp 95–97 °C. δ_H (DMSO): 8.36 (1H, d, J=7.3 Hz, H^1), 7.99–7.91 (2H, m, $H^{3,4}$), 7.87 (1H, m, H^2), 6.88–6.67 (3H, m, $H^{8,10,11}$), 4.34 (2H, s, NH_2), 2.95 (4H, m, CH_2NCH_2), 2.59 (3H, s, CH_3), 1.64 (4H, m, CH_2–CH_2–CH_2), 1.51 (2H, m, CH_2–CH_2–CH_2). Found, %: C 71.78, H 6.39, N 16.89. $C_{20}H_{22}N_4O$ (334.42). Requires, %: C 71.83, H 6.63, N 16.75.

4.5. Benzo[4,5]imidazo[2,1-*a*]phthalazines

Method A. BIPH preparation from aminophthalazinones. The mixture of 0.004 mol of aminophthalazinone and 15 g of PPA was heated to 130 °C and stirred for 10 min. On cooling it was diluted with water to 70 ml volume, neutralized with aqueous NaOH, and extracted with chloroform (3×30 ml). Combined extracts were dried over Na_2SO_4, filtered off, and evaporated. The residue was recrystallized from an appropriate solvent.

Method B. BIPH preparation from nitrophthalazinones. Mixture of 0.004 mol of nitrophthalazinone in 50 ml of 85% phosphoric acid was heated to 100 °C. Iron powder was added in small portions (to avoid foaming) with efficient stirring. After consumption of all the starting material (TLC control) the temperature was raised to 140 °C and the reaction mixture was stirred for 15 min. On cooling it was diluted with water to 400 ml, neutralized with aqueous NaOH, and extracted with chloroform (3×50 ml). Combined extracts were dried over Na_2SO_4, filtered off, and evaporated. The residue was recrystallized from an appropriate solvent.

4.5.1. 9-Chlorobenzo[4,5]imidazo[2,1-*a*]phthalazine 5a. *Method B*. From 1.21 g of nitrophthalazinone **3a** and 1.8 g of iron powder after recrystallization from 80% aqueous ethanol 0.69 g (68%) of the product **5a** were obtained as colorless crystals, mp 180–182 °C. ν_{max} (KBr): 1450, 1342, 1308, 1086, 762 cm^{-1}. δ_H (DMSO): 8.93 (1H, s, H^5), 8.62 (1H, d, J=7.8 Hz, H^1), 8.14 (1H, d, J=7.6 Hz, H^4), 8.06–7.87 (3H, m, $H^{2,3,8}$), 7.83 (1H, d, J=8.6 Hz, H^{11}), 7.43 (1H, dd, J=8.6 and 1.9 Hz, H^{10}). δ_C (DMSO): 144.30, 141.42, 140.14, 132.93, 131.27, 130.72, 128.25, 127.24, 124.72, 124.52, 124.20, 123.05, 120.62, 110.38. Found, %: C 66.17, H 3.20, N 16.75. $C_{14}H_8ClN_3$ (253.69). Requires, %: C 66.28, H 3.18, N 16.56.

4.5.2. 9-Chloro-5-methylbenzo[4,5]imidazo[2,1-*a*]phthalazine 5b. *Method A*. From aminophthalazinone **4a** (1.14 g) after recrystallization from 80% aqueous ethanol 0.65 g (61%) of the product **5b** were obtained as colorless crystals, mp 180–181 °C. ν_{max} (KBr): 1616, 1520, 1450, 1346, 1331, 1272, 806, 768 cm^{-1}. δ_H (DMSO): 8.56 (1H, d, J=7.6 Hz, H^1), 7.97–7.66 (5H, m, $H^{2,3,4,8,11}$), 7.30 (1H, d, J=8.4 Hz, H^{10}), 2.69 (3H, s, CH_3). δ_C (DMSO): 151.01, 141.98, 140.26, 133.17, 131.46, 131.32, 127.14, 124.83, 124.62, 124.46, 123.64, 120.95, 110.52, 19.49. Found, %: C 67.50, H 3.51, N 15.66. $C_{15}H_{10}ClN_3$ (267.72). Requires, %: C 67.30, H 3.77, N 15.70.

Method B. From nitrophthalazinone **3b** (1.26 g) and 1.3 g of iron powder after recrystallization from ethanol were obtained 0.62 g (58%) of product **5b**.

4.5.3. 9-Chloro-5-phenylbenzo[4,5]imidazo[2,1-*a*]phthalazine 5c. *Method A*. From aminophthalazinone **4b** (1.39 g) after recrystallization from chloroform–ethanol 0.84 g (64%) of product **5c** were obtained as colorless crystals, mp 223–225 °C. ν_{max} (KBr): 1449, 1359, 1344, 1273, 772, 710, 690 cm^{-1}. δ_H (DMSO): 8.66 (1H, d, J=7.8 Hz, H^1), 8.00–7.75 (5H, m, $H^{2,3,4,8,11}$), 7.75–7.56 (5H, m, C_6H_5), 7.40 (1H, d, J=8.6 Hz, H^{10}). δ_C (DMSO): 153.11, 141.66, 140.59, 134.54, 133.12, 131.69, 131.09, 129.78, 129.66, 128.60, 128.28, 127.48, 125.30, 125.14, 123.94, 120.96, 110.78. Found, %: C 72.70, H 3.43, N 12.87. $C_{20}H_{12}ClN_3$ (329.79). Requires, %: C 72.84, H 3.67, N 12.74.

Method B. From 1.51 g nitrophthalazinone **3c** and 1.5 g of iron powder after recrystallization from dichloromethane–methanol were obtained 0.91 g (69%) of product **5c**.

4.5.4. 9-Chloro-5-(4-methylphenyl)benzo[4,5]imidazo[2,1-*a*]phthalazine 5d. *Method B*. From nitrophthalazinone **3d** (1.57 g) and of 1.6 g of iron powder after recrystallization from chloroform–ethanol 0.76 g (55%) of product **5d** were obtained as yellow crystals, mp 241–243 °C. δ_H (DMSO): 8.72 (1H, d, J=7.8 Hz, H^1), 8.13–7.86 (5H, m, $H^{2,\ 3,\ 4,\ 8,\ 11}$), 7.68 (2H, d, J=7.5 Hz, CH–C(Ar)–CH), 7.52 (1H, m, H^{10}), 7.46 (2H, d, J=7.5 Hz, CH–C(Alk)–CH), 2.49 (3H, s, CH_3). δ_C ($CDCl_3$): 153.05, 141.62, 140.33, 139.47, 132.22, 131.65, 131.58, 130.12, 129.36, 129.00, 128.14, 125.39, 125.18, 124.12, 123.78, 120.27, 110.98, 21.02. Found, %: C 73.12, H 3.91, N 12.41. $C_{21}H_{14}ClN_3$ (343.82). Requires, %: C 73.36, H 4.10, N 12.22.

4.5.5. 9-Chloro-5-(4-chlorophenyl)benzo[4,5]imidazo[2,1-*a*]phthalazine 5e. *Method A*. From aminophthalazinone **4c** (1.53 g) after recrystallization from chloroform–ethanol 0.76 g (52%) of product **5e** were obtained as colorless crystals, mp 235–237 °C. δ_H (DMSO): 8.67 (1H, d, J=7.7 Hz, H^1), 8.06–7.95 (2H, m, ArH), 7.90–7.81 (3H, m, ArH), 7.77 (2H, d, J=7.9 Hz, CH–C(Cl)–CH), 7.66 (2H, d, J=7.9 Hz, CH–C(Ar)–CH), 7.44 (1H, dd, J=8.5 and 1.6 Hz, H^{10}). δ_C (DMSO): 151.78, 141.38, 140.14, 135.22, 132.78, 132.55, 131.37, 130.89, 130.50, 128.45, 127.75, 127.70, 125.03, 123.64, 123.50, 120.25, 110.63. Found, %: C 65.77, H 2.85, N 11.76. $C_{20}H_{11}Cl_2N_3$ (364.24). Requires, %: C 65.95, H 3.04, N 11.54.

Method B. From nitrophthalazinone **3e** (1.65 g) and 2.5 g of iron powder after recrystallization from chloroform–ethanol were obtained 0.73 g (50%) of product **5e**.

4.5.6. 9-Chloro-5-(4-ethylphenyl)benzo[4,5]imidazo[2,1-*a*]phthalazine 5f. *Method A*. From aminophthalazinone **4d** (1.50 g) after recrystallization from chloroform–ethanol 0.97 g (68%) of product **5f** were obtained as colorless crystals, mp 195–197 °C. δ_H (DMSO): 8.68 (1H, d, J=7.8 Hz, H^1), 8.02–7.72 (5H, m, $H^{2,\ 3,\ 4,\ 8,\ 11}$), 7.64 (2H, d, J=7.8 Hz, CH–C(Ar)–CH), 7.46–7.36 (3H, m, H^{10}, CH–C(Alk)–CH), 2.80 (2H, q, J=7.4 Hz, CH_2), 1.35 (3H, t, J=7.4 Hz, CH_3). δ_C (DMSO): 152.70, 145.23, 141.25, 140.31, 132.52, 131.74, 131.44, 130.46, 129.49, 127.96, 127.67, 127.30, 125.19, 124.76, 123.77, 120.52, 110.49, 28.18, 15.29. Found, %: C 73.76, H 4.37, N 11.97. $C_{22}H_{16}ClN_3$ (357.85). Requires, %: C 73.84, H 4.51, N 11.74.

Method B. From nitrophthalazinone **3f** (1.62 g) and 2.4 g of iron powder after recrystallization from ethanol were obtained 0.89 g (62%) of product **5f**.

4.5.7. 9-Chloro-5-(3,4-dimethylphenyl)benzo[4,5]imidazo[2,1-*a*]phthalazine 5g. *Method A*. From aminophthalazinone **4e** (1.50 g) after recrystallization from chloroform–ethanol 1.00 g (70%) of product **5g** were obtained as colorless crystals, mp 203–205 °C. δ_H (DMSO): 8.66 (1H, d, J=7.8 Hz, H^1), 7.99 (1H, d, J=1.8 Hz, H^8), 7.97–7.72 (4H, m, $H^{2,\ 3,\ 4,\ 11}$), 7.41 (1H, dd, J=8.5 and 1.8 Hz, H^{10}), 7.49–7.29 (3H, m, $(CH_3)_2$–C_6H_3), 2.39 (6H, s, $2CH_3$). δ_C (DMSO): 153.93, 142.36, 141.23, 138.82, 137.42, 133.75, 132.76, 132.31, 131.84, 131.46, 130.36, 129.14, 128.04, 127.93, 125.75, 124.72, 124.46, 121.74, 111.39, 20.18, 20.09. Found, %: C 73.63, H 4.34, N 11.94. $C_{22}H_{16}ClN_3$ (357.85). Requires, %: C 73.84, H 4.51, N 11.74.

Method B. From nitrophthalazinone **3g** (1.62 g) and 2.4 g of iron powder after recrystallization from ethanol were obtained 1.22 g (85%) of product **5g**.

4.5.8. 9-Chloro-5-(2,4-dimethylphenyl)benzo[4,5]imidazo[2,1-*a*]phthalazine 5h. *Method B*. From nitrophthalazinone **3h** (1.62 g) and 2.4 g of iron powder after recrystallization from ethanol 0.47 g (33%) of product **5h** were obtained as colorless crystals, mp 142–144 °C. δ_H (DMSO): 8.69 (1H, d, J=7.9 Hz, H^1), 8.05–7.89 (3H, m, $H^{2,\ 3,\ 8}$), 7.84 (1H, d, J=8.8 Hz, H^{11}), 7.73 (1H, m, $H^{3\ or\ 2}$), 7.50 (1H, d, J=8.0 Hz, H^4), 7.40 (1H, dd, J=8.8 and 1.8 Hz, H^{10}), 7.33–7.13 (3H, m, $(CH_3)_2$–C_6H_3), 2.45 (3H, s, 2′-CH_3), 2.14 (3H, s, 4′-CH_3). δ_C (DMSO): 153.00, 141.29, 140.30, 138.63, 136.16, 132.62, 131.46, 130.89, 130.77, 130.59, 129.52, 127.70, 127.35, 126.19, 124.96, 124.72, 124.42, 123.68, 120.57, 110.58, 20.86, 19.31. Found, %: C 73.84, H 4.42, N 11.89. $C_{22}H_{16}ClN_3$ (357.85). Requires, %: C 73.84, H 4.51, N 11.74.

4.5.9. 9-Chloro-5-(2,5-dimethylphenyl)benzo[4,5]imidazo[2,1-*a*]phthalazine 5i. *Method B*. From nitrophthalazinone **3i** (1.62 g) and 2.4 g of iron powder after recrystallization from ethanol 0.95 g (66%) of product **5i** were obtained as colorless crystals, mp 160–162 °C. δ_H (DMSO): 8.71 (1H, d, J=8.0 Hz, H^1), 8.02 (1H, d, J=1.8 Hz, H^8), 8.00 (1H, m, $H^{2\ or\ 3}$), 7.84 (1H, d, J=8.5 Hz, H^{11}), 7.78 (1H, m, $H^{3\ or\ 2}$), 7.53 (1H, d, J=8.0 Hz, H^4), 7.44 (1H, dd, J=8.5 and 1.8 Hz, H^{10}), 7.32–7.19 (3H, m, $(CH_3)_2$–C_6H_3), 2.40 (3H, s, 2′-CH_3), 2.11 (3H, s, 5′-CH_3). δ_C (DMSO): 154.31, 142.58, 141.23, 135.91, 134.55, 134.32, 134.20, 132.40, 132.31, 131.14, 131.06, 128.91, 128.08, 125.92, 125.61, 125.22, 124.55, 121.84, 111.61, 21.31, 19.74. Found, %: C 73.76, H 4.35, N 11.93. $C_{22}H_{16}ClN_3$ (357.85). Requires, %: C 73.84, H 4.51, N 11.74.

4.5.10. 5-Methylbenzo[4,5]imidazo[2,1-*a*]phthalazine 7a. *Method B*. From nitrophthalazinone **6a** (1.12 g) and 1.6 g of iron powder after recrystallization from 80% aqueous methanol 0.59 g (63%) of product **7a** were obtained as colorless crystals, mp 159–161 °C (lit. mp 163 °C[1]). ν_{max} (KBr): 1522, 1450, 1348, 1334, 1240, 743 cm^{-1}. δ_H ($CDCl_3$): 8.68 (1H, d, J=7.4 Hz, H^1), 7.99 (1H, d, J=7.2, H^4), 7.97–7.84 (2H, m, $H^{8,\ 11}$), 7.81 (1H, d, J=7.6 Hz, H^2), 7.68 (1H, m, H^3), 7.52–7.35 (2H, m, $H^{9,\ 10}$), 2.79 (3H, s, CH_3). δ_C (DMSO): 149.64, 141.42, 140.64, 132.44, 130.77, 130.47, 126.44, 124.50, 124.22, 124.04, 123.31, 122.16, 119.29, 110.51, 19.19. Found, %: C 77.35, H 4.59, N 18.20. $C_{15}H_{11}N_3$ (233.28). Requires, %: C 77.23, H 4.75, N 18.01.

4.5.11. 10-Amino-5-methylbenzo[4,5]imidazo[2,1-*a*]phthalazine 7b. *Method B*. From nitrophthalazinone **6b** (1.30 g) and 1.9 g of iron powder after recrystallization from chloroform–ethanol 0.56 g (58%) of product **7b** were obtained as colorless crystals, mp >270 °C (dec). ν_{max} (KBr): 3395, 3311, 3184, 1627, 1519, 1443, 1349, 1162, 762, 689 cm^{-1}. δ_H (DMSO): 8.55 (1H, d, J=7.7 Hz, H^1),

8.05 (1H, d, J=7.7 Hz, H^4), 7.89 (1H, m, $H^{2\ or\ 3}$), 7.76 (1H, m, $H^{3\ or\ 2}$), 7.67 (1H, d, J=8.6 Hz, H^8), 6.96 (1H, s, H^{11}), 6.78 (1H, d, J=8.6 Hz, H^9), 4.33 (2H, s, NH_2), 2.82 (3H, s, CH_3). δ_C (DMSO): 148.34, 146.18, 143.07, 140.08, 132.08, 129.72, 126.21, 124.40, 123.81, 123.66, 122.94, 112.83, 110.49, 101.33, 19.10. Found, %: C 72.48, H 4.61, N 22.32. $C_{15}H_{12}N_4$ (248.29). Requires, %: C 72.56, H 4.87, N 22.57.

4.5.12. 5-(4-Chlorophenyl)benzo[4,5]imidazo[2,1-*a*]-phthalazine 7c. *Method B*. From nitrophthalazinone **6c** (1.51 g) and 1.5 g of iron powder after recrystallization from chloroform–ethanol 0.75 g (57%) of product **7c** were obtained as yellow crystals, mp 217–219 °C. δ_H (DMSO): 8.74 (1H, d, J=7.9 Hz, H^1), 8.06–7.37 (11H, m, ArH). δ_C (DMSO): 152.43, 142.71, 141.60, 135.45, 134.43, 134.03, 132.57, 131.90, 129.60, 128.91, 126.04, 125.70, 124.58, 123.69, 120.55, 111.81. Found, %: C 72.81, H 3.47, N 12.94. $C_{20}H_{12}ClN_3$ (329.79). Requires, %: C 72.84, H 3.67, N 12.74.

4.5.13. 5-Methyl-9-morpholinobenzo[4,5]imidazo[2,1-*a*]-phthalazine 10a. *Method A*. From aminophthalazinone **9a** (1.34 g) after recrystallization from 80% aqueous ethanol 0.95 g (75%) of product **10a** were obtained as colorless crystals, mp 199–201 °C. ν_{max} (KBr): 1613, 1494, 1448, 1218, 1126, 908 cm^{-1}. δ_H (DMSO): 8.52 (1H, d, J=7.5 Hz, H^1), 8.11–7.74 (3H, m, $H^{2,\ 3,\ 4}$), 7.68 (1H, dd, J=9.0 and 2.0 Hz, H^{11}), 7.34 (1H, s, H^8), 7.17 (1H, d, J=9.0 Hz, H^{10}), 3.82 (4H, s, CH_2OCH_2), 3.22 (4H, m, CH_2NCH_2), 2.80 (3H, s, CH_3). δ_C (DMSO): 151.31, 148.46, 139.28, 133.30, 132.59, 131.29, 131.09, 127.19, 124.41, 123.53, 118.51, 116.87, 95.75, 66.22, 49.77, 19.48. Found, %: C 71.61, H 5.58, N 17.77. $C_{19}H_{18}N_4O$ (318.38). Requires, %: C 71.68, H 5.70, N 17.60.

Method B. From nitrophthalazinone **8a** (1.47 g) and 1.5 g of iron powder after recrystallization from ethanol were obtained 0.88 g (69%) of product **10a**.

4.5.14. 5-Methyl-9-pyrrolidinobenzo[4,5]imidazo[2,1-*a*]-phthalazine 10b. *Method B*. From nitrophthalazinone **8b** (1.40 g) and 1.4 g of iron powder after recrystallization from ethanol 0.72 g (59%) of product **10b** were obtained as yellow crystals, mp 250–252 °C. δ_H (DMSO): 8.52 (1H, d, J=7.6 Hz, H^1), 8.13 (1H, d, J=7.6 Hz, H^4), 7.96 (1H, m, $H^{2\ or\ 3}$), 7.82 (1H, m, $H^{3\ or\ 2}$), 7.71 (1H, d, J=8.3 Hz, H^{11}), 6.92–6.81 (2H, m, $H^{8,\ 10}$), 3.33 (4H, s, CH_2NCH_2), 2.82 (3H, s, CH_3) 2.02 (4H, m, CH_2CH_2). δ_C ($CDCl_3$): 148.40, 144.89, 139.09, 133.43, 132.34, 131.69, 128.78, 125.47, 123.84, 123.00, 119.62, 111.95, 90.48, 47.97, 25.13, 19.19. Found, %: C 75.02, H 5.75, N 18.70. $C_{19}H_{18}N_4$ (302.38). Requires, %: C 75.47, H 6.00, N 18.53.

4.5.15. 5-Methyl-9-piperidinobenzo[4,5]imidazo[2,1-*a*]-phthalazine 10c. *Method A*. From aminophthalazinone **9b** (1.34 g) after recrystallization from 80% aqueous ethanol 1.10 g (87%) of product **10c** were obtained as colorless crystals, mp 175–177 °C. δ_H ($CDCl_3$): 8.58 (1H, d, J=8.1 Hz, H^1), 7.85–7.52 (4H, m, $H^{2,\ 3,\ 4,\ 11}$), 7.41 (1H, d, J=1.9 Hz, H^8), 7.18 (1H, dd, J=8.9 and 1.9 Hz, H^{10}), 3.22 (4H, m, CH_2NCH_2), 2.72 (3H, s, CH_3), 1.76 (4H, m, $CH_2CH_2CH_2$), 1.58 (2H, m, $CH_2CH_2CH_2$). δ_C ($CDCl_3$): 148.96, 148.61, 139.90, 135.57, 131.64, 131.52, 129.07, 125.39, 125.05, 123.78, 123.02, 119.29, 117.38, 96.45, 51.61, 25.54, 23.80, 19.03. Found, %: C 75.45, H 6.16, N 17.87. $C_{20}H_{20}N_4$ (316.41). Requires, %: C 75.92, H 6.37, N 17.71.

Method B. From nitrophthalazinone **8c** (1.34 g) and 1.3 g of iron powder after recrystallization from ethanol were obtained 0.57 g (45%) of product **10c**.

4.5.16. 5-Methyl-9-piperazinobenzo[4,5]imidazo[2,1-*a*]-phthalazine 10d. *Method B*. From nitrophthalazinone **8d** (1.46 g) and 1.5 g of iron powder after recrystallization from chloroform–ethanol 1.02 g (81%) of product **10d** were obtained as yellow crystals, mp 262–264 °C. δ_H ($CDCl_3$): 8.68 (1H, d, J=7.8 Hz, H^1), 7.92 (1H, d, J=7.8 Hz, H^4), 7.89–7.64 (3H, m, $H^{2,\ 3,\ 11}$), 7.49 (1H, d, J=1.8 Hz, H^8), 7.22 (1H, dd, J=9.0 and 1.8 Hz, H^{10}), 3.26 (4H, m, CH_2NCH_2), 3.08 (4H, m, CH_2NHCH_2), 2.84 (3H, s, CH_3), 1.75 (1H, s, NH). δ_C ($CDCl_3$): 149.10, 148.79, 140.53, 136.25, 132.08, 131.90, 129.56, 125.83, 125.51, 124.30, 123.52, 119.82, 117.03, 96.62, 51.71, 46.10, 19.42. Found, %: C 71.33, H 5.90, N 22.25. $C_{19}H_{19}N_5$ (317.40). Requires, %: C 71.90, H 6.03, N 22.06.

4.5.17. 9-Morpholino-5-phenylbenzo[4,5]imidazo[2,1-*a*]-phthalazine 10e. *Method B*. From nitrophthalazinone **8e** (1.71 g) and 1.7 g of iron powder after recrystallization from toluene–petroleum ether 1.16 g (76%) of product **10e** were obtained as yellow crystals, mp 223–225 °C. ν_{max} (KBr): 1612, 1495, 1447, 1220, 1122, 960, 908, 771, 766 cm^{-1}. δ_H ($CDCl_3$): 8.71 (1H, d, J=7.9 Hz, H^1), 7.89−7.46 (10H, m, $H^{2,\ 3,\ 4,\ 8,\ 11}$, C_6H_5), 7.19 (1H, dd, J=9.0 and 1.8 Hz, H^{10}), 3.85 (4H, m, CH_2OCH_2), 3.21 (4H, m, CH_2NCH_2). δ_C ($CDCl_3$): 152.31, 148.13, 140.25, 136.53, 134.95, 132.12, 131.99, 129.63, 129.40, 129.26, 128.38, 128.00, 125.93, 123.62, 123.43, 119.92, 116.58, 96.59, 66.67, 50.41. Found, %: C 75.59, H 5.33, N 14.91. $C_{24}H_{20}N_4O$ (380.45). Requires, %: C 75.77, H 5.30, N 14.73.

4.5.18. 5-Phenyl-9-pyrrolidinobenzo[4,5]imidazo[2,1-*a*]-phthalazine 10f. *Method B*. From nitrophthalazinone **8f** (1.65 g) and 1.7 g of iron powder after recrystallization from chloroform–ethanol 0.91 g (62%) of product **10f** were obtained as yellow crystals, mp >270 °C. δ_H ($CDCl_3$): 8.81 (1H, d, J=8.1 Hz, H^1), 7.93–7.49 (9H, m, $H^{2,\ 3,\ 4,\ 11}$, C_6H_5), 7.11 (1H, d, J=1.8 Hz, H^8), 6.94 (1H, dd, J=8.6 and 1.8 Hz, H^{10}), 3.40 (4H, m, CH_2NCH_2), 2.05 (4H, m, CH_2CH_2). δ_C ($CDCl_3$): 151.95, 145.20, 139.02, 135.24, 133.79, 132.74, 132.10, 129.71, 129.71, 129.23, 128.98, 128.43, 128.43, 128.01, 126.25, 123.49, 123.30, 119.84, 112.51, 91.02, 48.17, 25.34. Found, %: C 78.77, H 5.22, N 15.50. $C_{24}H_{20}N_4$ (364.45). Requires, %: C 79.10, H 5.53, N 15.37.

4.5.19. 5-Phenyl-9-piperidinobenzo[4,5]imidazo[2,1-*a*]-phthalazine 10g. *Method B*. From nitrophthalazinone **8g** (1.70 g) and 1.7 g of iron powder after recrystallization from chloroform–ethanol 0.98 g (65%) of product **10g** were obtained as yellow crystals, mp 230–232 °C. δ_H ($CDCl_3$): 8.76 (1H, d, J=8.3 Hz, H^1), 7.90–7.52 (10H, m, $H^{2,\ 3,\ 4,\ 8,\ 11}$, C_6H_5), 7.26 (1H, dd, J=8.0 and 2.1 Hz, H^{10}), 3.24 (4H, m, CH_2NCH_2), 1.74 (4H, m, $CH_2CH_2CH_2$), 1.58 (2H, m, $CH_2CH_2CH_2$). δ_C ($CDCl_3$): 152.24, 149.39,

140.07, 136.24, 135.16, 132.16, 129.74, 129.28, 128.46, 128.06, 126.10, 123.65, 123.49, 119.75, 117.99, 97.05, 51.88, 25.83, 24.12. Found, %: C 78.83, H 5.71, N 14.94. $C_{25}H_{22}N_4$ (378.48). Requires, %: C 79.34, H 5.86, N 14.80.

4.5.20. 5-(4-Methylphenyl)-9-morpholinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10h. *Method B*. From nitrophthalazinone **8h** (1.77 g) and 1.8 g of iron powder after recrystallization from chloroform–ethanol 0.79 g (50%) of product **10h** were obtained as yellow crystals, mp 188–190 °C. δ_H ($CDCl_3$): 8.73 (1H, d, J=7.9 Hz, H^1), 7.92–7.78 (3H, m, $H^{2\ or\ 3,\ 4,\ 11}$), 7.67–7.55 (3H, m, $H^{3\ or\ 2}$, CH–C(Ar)–CH), 7.51 (1H, d, J=1.9 Hz, H^8), 7.37 (2H, d, J=7.6 Hz, CH–C(Alk)–CH), 7.20 (1H, dd, J=8.8 and 1.9 Hz, H^{10}), 3.88 (4H, m, CH_2OCH_2), 3.22 (4H, m, CH_2NCH_2), 2.46 (3H, s, CH_3). δ_C ($CDCl_3$): 152.56, 148.23, 140.45, 139.45, 136.65, 132.19, 129.60, 129.51, 129.15, 128.21, 126.05, 123.89, 123.58, 120.00, 116.70, 96.79, 66.80, 50.58, 21.24. Found, %: C 76.02, H 5.35, N 14.42. $C_{25}H_{22}N_4O$ (394.48). Requires, %: C 76.12, H 5.62, N 14.20.

4.5.21. 5-(4-Methylphenyl)-9-pyrrolidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10i. *Method B*. From nitrophthalazinone **8i** (1.70 g) and 1.7 g of iron powder after recrystallization from chloroform–ethanol 1.10 g (73%) of product **10i** were obtained as yellow crystals, mp 238–240 °C. δ_H ($CDCl_3$): 8.74 (1H, d, J=8.0 Hz, H^1), 7.92–7.78 (3H, m, $H^{2\ or\ 3,\ 4,\ 11}$), 7.70–7.55 (3H, m, $H^{3\ or\ 2}$, CH–C(Ar)–CH), 7.39 (2H, d, J=7.5 Hz, CH–C(Alk)–CH), 7.11 (1H, d, J=1.8 Hz, H^8), 6.90 (1H, dd, J=8.8 and 1.8 Hz, H^{10}), 3.40 (4H, m, CH_2NCH_2), 2.49 (3H, s, CH_3), 2.05 (4H, m, CH_2CH_2). δ_C ($CDCl_3$): 151.08, 144.14, 138.24, 137.85, 132.35, 131.62, 131.25, 130.99, 128.56, 128.05, 127.95, 126.99, 125.00, 122.56, 122.32, 118.60, 111.45, 90.00, 47.06, 24.24, 20.13. Found, %: C 79.04, H 5.52, N 14.93. $C_{25}H_{22}N_4$ (378.48). Requires, %: C 79.34, H 5.86, N 14.80.

4.5.22. 5-(4-Methylphenyl)-9-piperidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10j. *Method B*. From nitrophthalazinone **8j** (1.76 g) and 1.8 g of iron powder after recrystallization from chloroform–ethanol 0.91 g (58%) of product **10j** were obtained as yellow crystals, mp 205–207 °C. ν_{max} (KBr): 2935, 2851, 1666, 1601, 1501, 1327, 1103 cm^{-1}. δ_H ($CDCl_3$): 8.75 (1H, d, J=7.9 Hz, H^1), 7.95–7.78 (3H, m, $H^{2\ or\ 3,\ 4,\ 11}$), 7.68–7.58 (3H, m, $H^{3\ or\ 2}$, CH–C(Ar)–CH), 7.61 (1H, d, J=1.9 Hz, H^8), 7.39 (2H, d, J=7.6 Hz, CH–C(Alk)–CH), 7.27 (1H, dd, J=7.9 and 1.9 Hz, H^{10}), 3.24 (4H, m, CH_2NCH_2), 2.49 (3H, s, CH_3), 1.76 (4H, m, $CH_2CH_2CH_2$), 1.60 (2H, m, $CH_2CH_2CH_2$). δ_C ($CDCl_3$): 152.32, 149.36, 140.14, 139.34, 136.26, 132.31, 132.10, 129.63, 129.28, 129.12, 128.14, 126.15, 123.81, 123.48, 119.72, 117.97, 97.11, 51.91, 25.88, 24.13, 21.24. Found, %: C 79.33, H 5.74, N 14.41. $C_{26}H_{24}N_4$ (392.51). Requires, %: C 79.56, H 6.16, N 14.27.

4.5.23. 5-(4-Chlorophenyl)-9-morpholino-benzo[4,5]-imidazo[2,1-*a*]phthalazine 10k. *Method B*. From nitrophthalazinone **8k** (1.85 g) and 1.9 g of iron powder after recrystallization from chloroform–ethanol 1.41 g (85%) of product **10k** were obtained as yellow crystals, mp 220–222 °C. δ_H ($CDCl_3$): 8.71 (1H, d, J=7.7 Hz, H^1), 7.89–7.73 (3H, m, $H^{2,\ 4,\ 11}$), 7.67 (2H, d, J=7.7 Hz, CH–C(Cl)–CH), 7.62–7.45 (3H, m, H^3, CH–C(Ar)–CH), 7.46 (1H, d, J=1.8 Hz, H^8), 7.20 (1H, dd, J=8.9 and 1.8 Hz, H^{10}), 3.88 (4H, m, CH_2OCH_2), 3.23 (4H, m, CH_2NCH_2). δ_C ($CDCl_3$): 151.21, 148.30, 140.17, 136.56, 135.60, 133.44, 132.37, 131.95, 131.06, 129.56, 128.74, 127.66, 125.98, 123.62, 123.36, 120.03, 116.75, 96.52, 66.75, 50.45. Found, %: C 69.45, H 4.42, N 13.71. $C_{24}H_{19}ClN_4O$ (414.90). Requires, %: C 69.48, H 4.62, N 13.50.

4.5.24. 5-(4-Chlorophenyl)-9-pyrrolidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10l. *Method B*. From nitrophthalazinone **8l** (1.79 g) and 1.8 g of iron powder after recrystallization from chloroform–ethanol 1.16 g (73%) of product **10l** were obtained as yellow crystals, mp 234–236 °C. δ_H ($CDCl_3$): 8.72 (1H, d, J=8.0 Hz, H^1), 7.89–7.75 (3H, m, $H^{2\ or\ 3,\ 4,\ 11}$), 7.70 (2H, d, J=7.4 Hz, CH–C(Cl)–CH), 7.65–7.52 (3H, m, H^3, CH–C(Ar)–CH), 7.06 (1H, s, H^8), 6.90 (1H, d, J=8.6 Hz, H^{10}), 3.39 (4H, m, CH_2NCH_2), 2.04 (4H, m, CH_2CH_2). δ_C ($CDCl_3$): 150.71, 145.24, 138.90, 135.46, 133.90, 133.74, 132.72, 132.19, 131.12, 129.02, 128.73, 127.59, 126.34, 123.41, 123.16, 119.98, 112.58, 90.89, 48.16, 25.34. Found, %: C 72.15, H 4.62, N 14.22. $C_{24}H_{19}ClN_4$ (398.90). Requires, %: C 72.27, H 4.80, N 14.05.

4.5.25. 5-(4-Chlorophenyl)-9-piperidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10m. *Method B*. From nitrophthalazinone **8m** (1.84 g) and 1.8 g of iron powder after recrystallization from chloroform–ethanol 1.06 g (64%) of product **10m** were obtained as yellow crystals, mp 160–162 °C. δ_H ($CDCl_3$): 8.73 (1H, d, J=7.8 Hz, H^1), 7.90–7.75 (3H, m, $H^{2\ or\ 3,\ 4,\ 11}$), 7.72–7.60 (3H, m, $H^{3\ or\ 2}$, CH–C(Cl)–CH), 7.51 (2H, d, J=7.7 Hz, CH–C(Ar)–CH), 7.41 (1H, d, J=1.8 Hz, H^8), 7.31 (1H, dd, J=8.8 Hz, H^{10}), 3.23 (4H, m, CH_2NCH_2), 1.75 (4H, m, $CH_2CH_2CH_2$), 1.59 (2H, m, $CH_2CH_2CH_2$). δ_C ($CDCl_3$): 151.04, 149.52, 139.90, 136.19, 135.53, 133.62, 132.31, 132.06, 131.11, 129.40, 128.72, 127.61, 126.14, 123.62, 123.36, 119.80, 118.05, 96.89, 51.81, 25.84, 24.08. Found, %: C 72.65, H 5.01, N 13.75. $C_{25}H_{21}ClN_4$ (412.93). Requires, %: C 72.72, H 5.13, N 13.57.

4.5.26. 5-(4-Chlorophenyl)-9-piperazinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10n. *Method B*. From nitrophthalazinone **8n** (1.84 g) and 1.8 g of iron powder after recrystallization from ethanol 1.04 g (63%) of product **10n** were obtained as yellow crystals, mp 216–218 °C. δ_H ($CDCl_3$): 8.72 (1H, d, J=7.9, H^1), 7.91–7.76 (3H, m, $H^{2\ or\ 3,\ 4,\ 11}$), 7.72–7.61 (3H, m, $H^{3\ or\ 2}$, CH–C(Cl)–CH), 7.56 (2H, d, J=8.5 Hz, CH–C(Ar)–CH), 7.48 (1H, d, J=2.0 Hz, H^8), 7.25 (1H, dd, J=8.6 and 2.0 Hz, H^{10}), 3.22 (4H, m, CH_2NCH_2), 3.07 (4H, m, CH_2NHCH_2), 1.71 (1H, s, NH). δ_C ($CDCl_3$): 151.14, 148.96, 140.10, 136.46, 135.60, 133.55, 132.37, 132.04, 131.09, 129.53, 128.76, 127.69, 126.09, 123.67, 123.38, 119.95, 117.31, 96.74, 51.59, 46.07. Found, %: C 69.40, H 4.87, N 17.08. $C_{24}H_{20}ClN_5$ (413.91). Requires, %: C 69.64, H 4.87, N 16.92.

4.5.27. 5-(4-Ethylphenyl)-9-piperidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10o. *Method B*. From nitrophthalazinone **8o** (1.82 g) and 1.8 g of iron powder after recrystallization from ethanol 1.07 g (66%) of product **10o**

were obtained as yellow crystals, mp 185–187 °C. δ_H (DMSO): 8.65 (1H, d, J=7.7 Hz, H^1), 7.91 (1H, m, $H^{2\ or\ 3}$), 7.82 (1H, d, J=7.2 Hz, H^4), 7.69 (1H, d, J=9.0 Hz, H^{11}), 7.68 (1H, m, $H^{3\ or\ 2}$), 7.62 (2H, d, J=7.5 Hz, CH–C(Ar)–CH), 7.45–7.36 (3H, m, H^8, CH–C(Alk)–CH), 7.18 (1H, dd, J=9.0 and 1.8 Hz, H^{10}), 3.21 (4H, m, CH_2NCH_2), 2.77 (2H, q, J=7.5 Hz, CH_2), 1.74 (4H, m, $CH_2CH_2CH_2$), 1.60 (2H, m, $CH_2CH_2CH_2$), 1.34 (3H, t, CH_3). δ_C (DMSO): 151.80, 144.92, 139.42, 136.05, 132.13, 131.52, 129.52, 127.79, 127.60, 125.67, 123.29, 119.43, 117.42, 97.04, 51.64, 28.19, 25.23, 23.60, 15.36. Found, %: C 79.55, H 6.01, N 13.92. $C_{27}H_{26}N_4$ (406.54). Requires, C 79.77, H 6.45, N 13.78.

4.5.28. 5-(3,4-Dimethylphenyl)-9-piperidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10p. *Method B*. From nitrophthalazinone **8p** (1.82 g) and 1.8 g of iron powder after recrystallization from ethanol 1.07 g (66%) of product **10p** were obtained as yellow crystals, mp 162–164 °C. δ_H (DMSO): 8.60 (1H, d, J=7.8 Hz, H^1), 7.90 (1H, m, $H^{2\ or\ 3}$), 7.83 (1H, d, J=8.1 Hz, H^4), 7.69 (1H, d, J=8.8 Hz, H^{11}), 7.68 (1H, m, $H^{3\ or\ 2}$), 7.49–7.28 (4H, m, H^8, $(CH_3)_2$–C_6H_3), 7.18 (1H, dd, J=8.8 and 2.0 Hz, H^{10}), 3.20 (4H, m, CH_2NCH_2), 2.39 (6H, s, $2CH_3$), 1.71 (4H, m, $CH_2CH_2CH_2$), 1.59 (2H, m, $CH_2CH_2CH_2$). δ_C (DMSO): 152.91, 149.65, 140.25, 138.47, 137.30, 136.56, 133.40, 133.21, 132.60, 131.42, 130.68, 130.26, 128.94, 127.97, 126.37, 124.13, 123.86, 120.56, 118.14, 96.93, 51.84, 26.28, 24.64, 20.14, 20.02. Found, %: C 79.62, H 5.91, N 13.95. $C_{27}H_{26}N_4$ (406.54). Requires, C 79.77, H 6.45, N 13.78.

4.5.29. 5-(2,5-Dimethylphenyl)-9-piperidinobenzo[4,5]-imidazo[2,1-*a*]phthalazine 10q. *Method B*. From nitrophthalazinone **8q** (1.82 g) and 1.8 g of iron powder after recrystallization from ethanol 0.82 g (57%) of product **10q** were obtained as yellow crystals, mp 220–222 °C. δ_H (DMSO): 8.63 (1H, d, J=7.8 Hz, H^1), 7.92 (1H, m, $H^{3\ or\ 2}$), 7.71 (1H, d, J=9.2 Hz, H^{11}), 7.68 (1H, m, $H^{2\ or\ 3}$), 7.43 (1H, d, J=8.2 Hz, H^4), 7.39 (1H, d, J=2.0 Hz, H^8), 7.31–7.20 (3H, m, $(CH_3)_2$–C_6H_3), 7.19 (1H, dd, J=9.2 and 2.0 Hz, H^{10}), 3.21 (4H, m, CH_2NCH_2), 2.40 (3H, s, 2′-CH_3), 2.11 (3H, s, 5′-CH_3), 1.72 (4H, m, $CH_2CH_2CH_2$), 1.58 (2H, m, $CH_2CH_2CH_2$). δ_C (DMSO): 153.24, 149.87, 140.34, 136.47, 135.85, 135.02, 134.24, 133.87, 133.72, 132.70, 131.12, 131.03, 130.84, 128.71, 126.27, 124.63, 123.96, 120.66, 118.18, 96.79, 51.76, 26.27, 24.72, 21.24, 19.65. Found, %: C 79.41, H 6.09, N 13.99. $C_{27}H_{26}N_4$ (406.54). Requires, C 79.77, H 6.45, N 13.78.

References and notes

1. Rowe, F. M.; Adams, D. A. W.; Peters, A. T.; Gillam, J. M. *J. Chem. Soc.* **1937**, 90–109.
2. Razvi, M.; Ramalingam, T. *Indian J. Chem., Sect. B* **1992**, *31B*, 788–789.
3. Shubin, K. M.; Kuznetsov, V. A.; Galishev, V. A. *Tetrahedron Lett.* **2004**, *45*, 1407–1408.
4. Mangini, A.; Deliddo, C. *Gazz. Chim. Ital.* **1933**, *63*, 612–629.
5. Lindley, J. M.; McRobbie, I. M.; Meth-Cohn, O.; Suschitzki, H. *J. Chem. Soc., Perkin Trans. 1* **1980**, 982–994.
6. Yakovlev, S. V.; Pavlova, L. A. *J. Org. Chem. USSR (Engl. Transl.)* **1988**, *24*, 2195–2197.
7. Runti, C.; Galimberti, S. *Ann. Chim. (Rome)* **1957**, *47*, 250–259.
8. Morgan, D. O.; Ollis, W. D.; Stanforth, S. P. *Tetrahedron* **2000**, *56*, 5523–5534.
9. Rowe, F. M.; Osborn, W. *J. Chem. Soc.* **1947**, 829–837.
10. Rowe, F. M.; Heath, G. M.; Patel, C. V. *J. Chem. Soc.* **1936**, 311–315.
11. Grimmett, M. R. *Imidazole and Benzimidazole Synthesis*; Academic: London, 1997; 265 p.