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FULL-LENGTH PAPER

One-pot, sequential four-component synthesis of benzo[*c*]pyrano[3,2-*a*]phenazine, bis-benzo[*c*]pyrano[3,2-*a*]phenazine and oxospiro benzo [*c*]pyrano[3,2-*a*]phenazine derivatives using 1,4-diazabicyclo[2.2.2]octane (DABCO) as an efficient and reusable solid base catalyst

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Abstract 1,4-Diazabicyclo[2.2.2]octane (DABCO) has been used as an efficient and reusable solid base catalyst for the one-pot, two-step, four-component synthesis of pyrano[3,2-*a*]phenazine derivatives by the condensation reaction of 2-hydroxy-1,4-naphthoquinone, 1,2-diamines, carbonyl compounds and alkylmalonates under conventional heating as well as microwave irradiation. This procedure has also been applied successfully for the synthesis of novel bis- benzo[*c*]pyrano[3,2-*a*]phenazine and oxospiro benzo[*c*]pyrano[3,2-*a*]phenazine derivatives. Using this procedure, all the products were obtained in good to excellent yields. The catalyst has been recovered and reused several times without any loss of reactivity.

Keywords Multi-component reactions · MCRs · 1,4-Diazabicyclo[2.2.2]octane · DABCO · Microwave irradiation · Pyrano[3,2-*a*]phenazines · Bis- benzo[*c*]pyrano[3,2-*a*]phenazines · Oxospiro benzo[*c*]pyrano[3,2-*a*]phenazines

Introduction

In the past few years, combinatorial methods using multi-component reactions (MCRs) have been closely examined as a fast and convenient solution for the synthesis of diverse classes of compounds [1,2]. MCRs have been steadily gaining importance in synthetic organic chemistry [1–3] because of their advantages in comparison with multi-step reactions according to environmental and economic considerations. Therefore, the design of novel MCRs has attracted great attention from research groups working in areas such as drug discovery and organic synthesis.

Naphthoquinone derivatives have been used as useful substrates in the synthesis of drug-like compounds. For example, b-lapachone [4,5] (Fig. 1a) shows good activity in order to obtain depletion of NADH and/or NADPH as well as ATP levels in biological oxidation processes. Besides, it is well known that the electron transport chains in metabolic pathways can be accomplished in the presence of naphthoquinone derivatives [6–10]. Phenazines are nitrogen-containing heterocycles that are the main core of many natural and synthetic organic materials [6–12]. They are structural components of various kinds of bacteria species [13,14]. Moreover, they have been used as dyestuffs, pesticides and antibiotics and show various pharmaceutical activities such as antimalarial [12], trypanocidal [15], fungicidal [16,17], antiplatet [18], antitumor, and antiphrastic [12]. Among various phenazine derivatives, polycyclic phenazine-type compounds (Fig. 1b) have optoelectric properties and have been applied for PLB proliferation as a substitute for plant growth regulators [19,20]. Benzo[*a*]phenazines that have a napthoquinone and phenazin backbone in their structures (Fig. 1c) show high activity as dual inhibitors of topoisomerase I and II and are useful as antitumor agents [21].

There is only one report for the synthesis of benzo[*c*] pyrano[3,2-*a*]phenazines in the literature using acidic conditions [22] that is limited to the synthesis of some benzo[*c*] pyrano[3,2-*a*]phenazines and is not suitable for acid-sensitive substrates. The corrosive nature of acetic acid (an important issue in industrial processes) and its high heat capacity and

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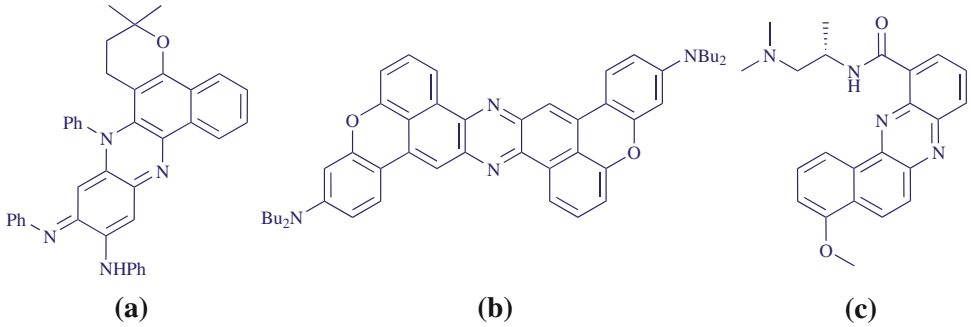
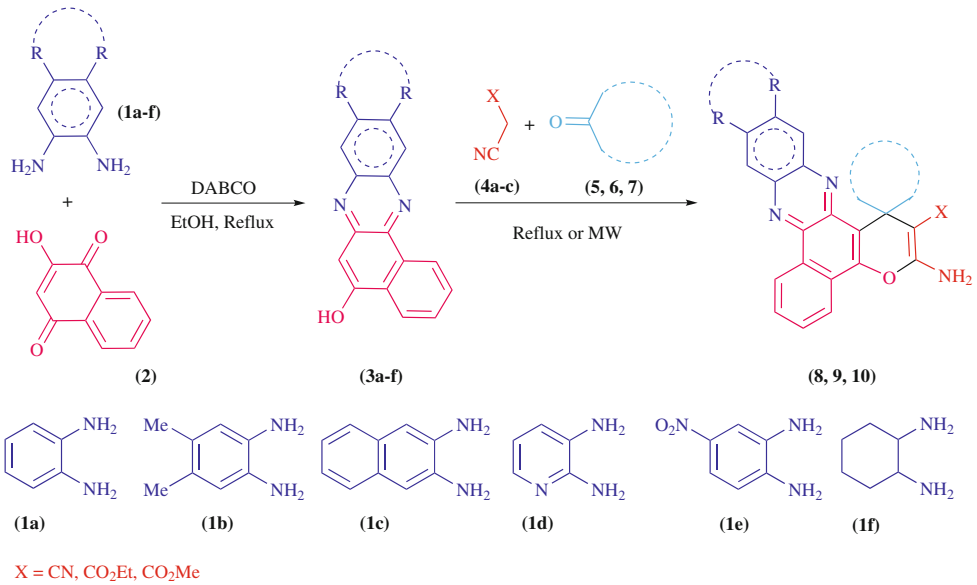


Fig. 1 Biological active compounds based on napthoquinone and phenazin derivatives



Scheme 1 The synthesis of 3-aminobenzo[*c*]pyrano[3,2-*a*]phenazine derivatives

high boiling point (requiring more energy for heating and evaporation) and also its flammability at the temperatures up to 40 °C [23,24] in this reported protocol, lead to the need of finding a practical, general, and environmentally benign synthetic process for the synthesis of a broad spectrum of pyrano[3,2-*a*]phenazine derivatives.

Considering the importance of naphthoquinone, phenazine, and pyran derivatives, and in continuation of our ongoing program for the synthesis of complex organic compounds based on green chemistry protocols [25–31], herein we wish to report a highly efficient method for the diversity-oriented synthesis of benzo[*c*]pyrano[3,2-*a*]phenazine, bis-benzo[*c*]pyrano[3,2-*a*]phenazine and oxospiro benzo[*c*]pyrano[3,2-*a*]phenazine derivatives via a one-pot, two-step condensation reaction in the presence of 1,4-diazabicyclo [2.2.2]octane (DABCO) as an efficient and reusable solid base catalyst under both conventional and microwave heating (Scheme 1).

Results and discussion

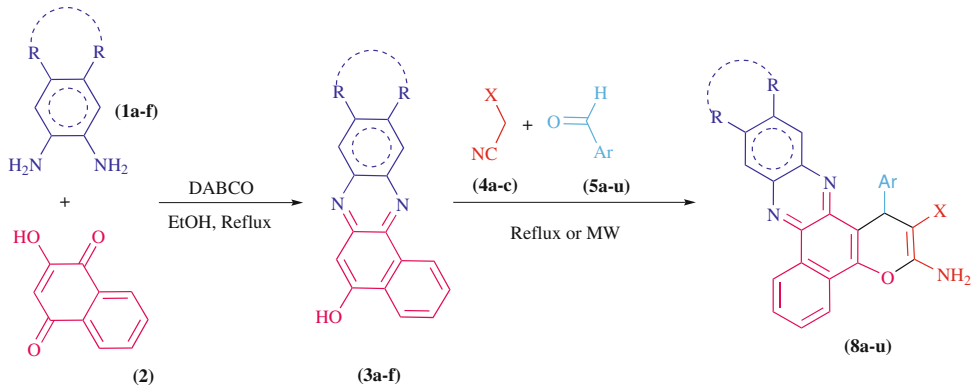
At first, benzene-1,2-diamine (**1a**, 1 mmol) and 2-hydroxy-1,4-naphthoquinone (**2a**, 1 mmol) were added to a 25- mL round-bottomed flask containing DABCO in ethanol under reflux conditions to form the corresponding phenazine (**3a**, 1 mmol). To find the best reaction conditions for the synthesis of the benzo[*c*]pyrano[3,2-*a*]phenazine, the condensation reaction between phenazine (**3a**), malononitrile (**4a**, 1 mmol), and benzaldehyde (**5a**, 1 mmol) in the presence of DABCO was selected as a model reaction and the yield and reaction time were monitored in different solvents and different molar ratios of DABCO at various temperatures. The obtained results have been summarized in Table 1. As it is shown in Table 1, higher yield and shorter reaction time were obtained when the reaction was carried out in the presence of 30 mol% of the catalyst in ethanol under reflux conditions (Table 1, entry 2).

In the next step, the scope and efficiency of the catalyst were explored under the optimized reaction conditions for the condensation of different phenazines with a broad range of structurally diverse aromatic aldehydes and alkylmalonates to furnish the related products (Scheme 2). The results are displayed in Table 2. The synthetic pathway for the synthesis of the titled compounds is consisting of two steps. At first, benzo[*a*]phenazin-5-ols are obtain from the condensation reaction of 1,2-diamines (**1a–f**) and

Table 1 Condensation reaction between 2-hydroxy-1,4-naphthoquinone (1 mmol), benzene-1,2-diamine (1 mmol), benzaldehyde (1 mmol), and malononitrile (1 mmol) under various conditions

Entry	Solvent	Reaction conditions	Time (h)	Yield[a] (%)
1	H_2O	Reflux, DABCO (30 mol%)	3.00	Trace
2	EtOH	Reflux, DABCO (30 mol%)	0.75	95
3	CH_3CN	Reflux, DABCO (30 mol%)	1.50	85
4	$(CH_3)_2CO$	Reflux, DABCO (30 mol%)	2.00	50
5	$CHCl_3$	Reflux, DABCO (30 mol%)	3.00	70
6	CH_2Cl_2	Reflux, DABCO (30 mol%)	2.00	80
7	DMF	100 °C, DABCO (30 mol%)	0.25	65
8	DMSO	100 °C, DABCO (30 mol%)	0.33	40
9	EtOH	RT, DABCO (30 mol%)	12.00	30
10	EtOH	40 °C, DABCO (30 mol%)	10.00	47
11	EtOH	50 °C, DABCO (30 mol%)	7.00	68
12	EtOH	60 °C, DABCO (30 mol%)	4.00	74
13	EtOH	Reflux, DABCO (10 mol%)	3.00	80
14	EtOH	Reflux, DABCO (20 mol%)	1.50	90

[a] Isolated yields



Scheme 2 The synthesis of 3-aminobenzo[*c*]pyrano[3, 2-*a*]phenazine derivatives via the reaction between 2-hydroxy-1,4-naphthoquinone (1 mmol), 1,2-diamine (1 mmol), aryl aldehyde (1 mmol), and malono derivatives (1 mmol) in the presence of DABCO (0.3 mmol) in EtOH under reflux condition or under microwave irradiation

2-hydroxy-1,4-naphthoquinone (**2**). Then, the resulting products are treated with alkylmalonates (**4a–c**) and carbonyl compounds (**5–7**) to afford the related benzo[*c*]pyrano[3, 2-*a*] phenazine derivatives as the desired products.

As it is clear from Table 2, various 1,2-diamine derivatives such as 4,5-dimethyl benzene-1,2-diamine, naphthalene-2,3-diamine, 4-nitrobenzene-1,2-diamine, pyridine-2,3-diamine and cyclohexane-1,2-diamine have been applied for the synthesis of benzo[*a*]phenazin-5-ols. The required times for the preparation of desired benzo[*a*]phenazin-5-ols in the presence of DABCO in ethanol under reflux condition in the case of benzene-1,2-diamine (**1a**) and 4,5-dimethyl benzene-1,2-diamine (**1b**) are 3 and 2 h, respectively. For other 1,2-diamine derivatives (**1c**, **1d**, **1e**, **1f**), this time is longer (10 h).

Recently many investigations have established the critical role of microwave energy as a means of rate enhancement in synthesis. Microwave irradiation often dramatically reduces reaction times. Moreover, microwave heating is able to minimize side reactions, increase yields, improve reproducibility, allow control of temperature and pressure, and even enable unaccessible reactions by conventional heating. Considering these facts, and in continuation of our recent efforts to introduce the microwave-enhanced methods in organic synthesis [32,33], we decided to examine our methodology under microwave irradiation. Under microwave conditions a considerable decrease of the reaction time was observed at 80 °C and 200 W irradiation. In order to perform a microwave-enhanced synthesis of the titled compounds, the phenazine (**3**) that was formed from the condensation reaction of 1,2-diamine (**1**) with 2-hydroxy-1,4-naphthoquinone (**2**) was transferred to a microwave vessel containing carbonyl compounds (**5–7**) and alkylmalonate derivatives (**4**) followed by microwave irradiation for selected times (Table 2). As it is clear from Table 2, the use of microwave irradiation vs conventional heating provides for a rate enhancement as we expect.

Table 2 Synthesis of 3-amino-1-aryl-1*H*-benzo[*c*]pyrano[3, 2 − *a*] phenazine derivatives from the reaction of 2-hydroxy-1,4-naphthoquinone (1 mmol), 1,2-diamine (1 mmol), aromatic aldehydes (1 mmol), and malono derivatives (1 mmol) in the presence of DABCO (0.3 mmol) in ethanol at reflux condition or under microwave irradiation

Entry	Diamin	Ar	X	Product	Conventional heating (Method A)		Microwave irradiation (Method B)	
					Time (h)	Yield[a] (%)	Time (min)	Yield[a] (%)
1	**1a**	C_6H_5	CN	**8a**	0.75	95	8	92
2	**1a**	4-F C_6H_5	CN	**8b**	1.00	95	10	90
3	**1a**	3-NO_2 C_6H_5	CO_2Et	**8c**	5.50	90	18	88
4	**1a**	3-Br C_6H_5	CO_2Me	**8d**	5.80	89	20	90
5	**1a**	4-Cl C_6H_5	CO_2Et	**8e**	5.00	91	20	91
6	**1a**	4-CF_3 C_6H_5	CN	**8f**	0.30	94	6	95
7	**1a**	3-OPh C_6H_5	CN	**8g**	0.50	87	7	90
8	**1a**	4-MeS C_6H_5	CN	**8h**	3.30	90	12	87
9	**1a**	1-Naphthyl	CN	**8i**	0.65	89	8	90
10	**1a**	2-Naphthyl	CN	**8j**	0.75	90	11	88
11	**1a**	3-Indolyl	CN	**8k**	5.30	60	16	70
12	**1a**	C_6H_5-CO	CN	**8l**	1.50	88	12	90
13	**1a**	2-Thienyl	CN	**8m**	2.50	90	15	90
14	**1a**	5-Me-2-thienyl	CN	**8n**	2.60	89	14	86
15	**1a**	3-Thienyl	CN	**8o**	0.60	92	10	91
16	**1a**	2-Furyl	CN	**8p**	3.00	86	18	88
17	**1a**	5-Me-2-furyl	CN	**8q**	3.00	91	15	90
18	**1a**	2-Pyrolyl	CN	**8r**	8.00	50	20	60
19	**1d**	2-NO_2-C_6H_5	CN	**8s**	13.00	73	25	78
20	**1e**	4-NO_2-C_6H_5	CN	**8t**	10.00	60	25	63
21	**1f**	3-Cl-C_6H_5	CN	**8u**	2.70	50	15	57

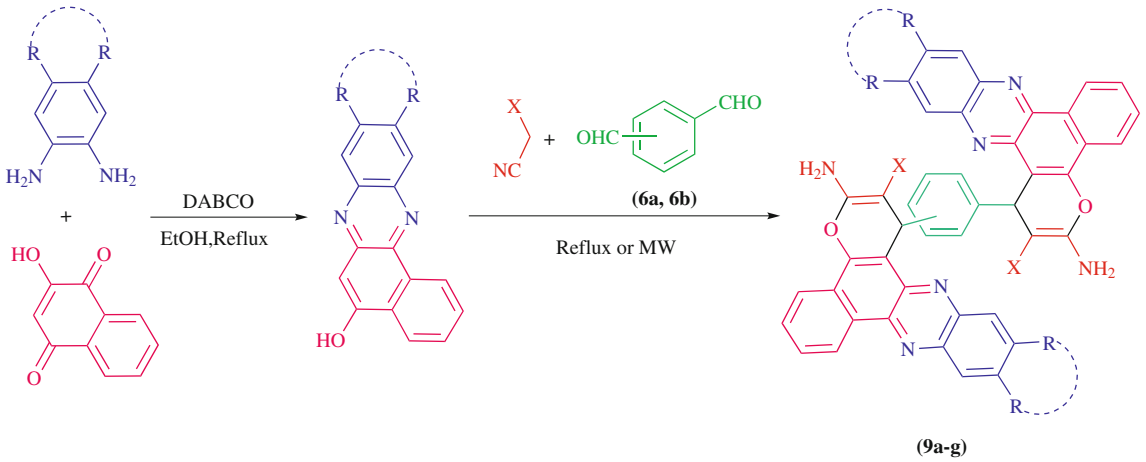
[a] Isolated yields

As shown in Table 2, a wide range of substituent patterns can be introduced in 3-amino-1*H*- benzo[*c*]pyrano[3, 2-*a*] phenazines. Electron-donating groups on the aromatic ring of aldehydes increased the rate of reaction, whereas electron-withdrawing substituents reduced the rate of reaction. Use of malononitrile leads to shorter reaction times and higher yields compared to application of other alkylmalonates such as ethyl cyanoacetate or methyl cyanoacetate. We also successfully applied acid sensitive heteroaromatic aldehydes and the related products were obtained without any by-products or side reactions.

Interestingly, this catalytic system was effectively used for the synthesis of complex structures of bis-3-amino-1*H*-benzo[*c*]pyrano[3, 2-*a*]phenazine derivatives (**9a**–**g**) from the condensation reaction between 2-hydroxy-1,4-naphtho quinone, 1,2-diamines, malono derivatives, and terphtalaldehyde or isophtalaldehyde for the first-time (Scheme 3). The reaction of 2 equivalents of 2-hydroxy-1,4-naphtho quinone, 1,2-diamines, and malono derivatives with 1 equivalent of dialdehyde proceeded rapidly to give the related compounds (**8a**–**g**) in desirable yields and the obtained results are summarized in Table 3.

After the successful synthesis of mono and bis 3-amino-1*H*-benzo[*c*]pyrano[3, 2-*a*]phenazines, this catalytic system was used for the synthesis of novel 3-amino spirobenzo[*c*] pyrano[3, 2-*a*]phenazine derivatives (Scheme 4). For this purpose, 2-hydroxy-1,4-naphthoquinone, 1,2-diamines and malono derivatives were condensed with isatin derivatives (**7a**–**d**) under optimized reaction conditions to afford the related products (Scheme 3). The obtained results are summarized in Table 4. As it is clear from this table, a broad spectrum of isatine derivatives have been used for the synthesis of the related spirocyclic compounds in good to excellent yields.

In another study, the condensation of benzene-1,2-diamine (1 mmol) (**1a**), 2-hydroxy-1,4-naphthoquinone (1 mmol) (**2**) with benzaldehyde (1 mmol) (**5a**) and malononitrile (1 mmol) (**4a**) were tested in the presence of recovered DABCO (0.3 mmol) in ethanol (5 mL) at reflux condition to establish the reusability of the catalyst (Table 5). After completion of the reaction, as monitored by TLC, the reaction mixture was allowed to cool to room temperature. The solid product was filtered, dried, and subsequently recrystallized from hot ethanol. In order to recover the catalyst, ethanol was evap-



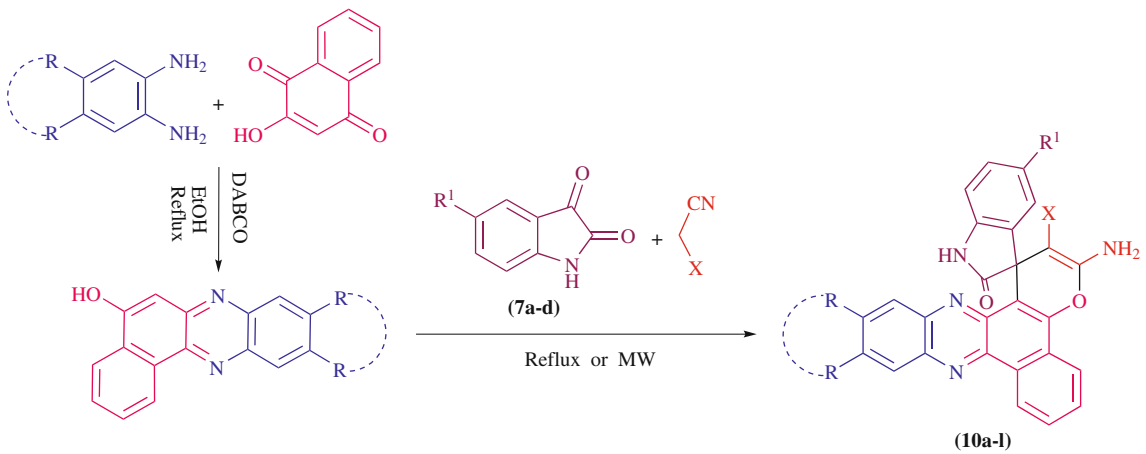
(6a): 4-CHO-C_6H_4, **(6b):** 3-CHO-C_6H_4

Scheme 3 The synthesis of bis 3-amino-1*H*-benzo[*c*]pyrano[3, 2-*a*]phenazine derivatives via the reaction between 2-hydroxy-1,4-naphthoquinone (2 mmol), 1,2-diamine (2 mmol), terephtalaldehyde or isophtalaldehyde (1 mmol), and malono derivatives (2 mmol) in the presence of DABCO (0.6 mmol) in EtOH under reflux condition or under microwave irradiation

Table 3 The synthesis of bis 3-amino-1*H*-benzo[*c*]pyrano[3, 2 − *a*]phenazine derivatives via the reaction between 2-hydroxy-1,4-naphthoquinone (2 mmol), 1,2-diamine (2 mmol), terephtalaldehyde or isophtalaldehyde (1 mmol), and malono derivatives (2 mmol) in the presence of DABCO (0.6 mmol) in EtOH under reflux condition and under microwave irradiation

Entry	Diamin	Ar	X	Product	Conventional heating (Method A)		Microwave irradiation (Method B)	
					Time (h)	Yield[a] (%)	Time (min)	Yield[a] (%)
1	**1a**	4-CHO-C_6H_4	CN	**9a**	0.80	89	10	92
2	**1a**	3-CHO-C_6H_4	CN	**9b**	0.90	88	10	90
3	**1a**	4-CHO-C_6H_4	CO_2Et	**9c**	7.50	75	23	88
4	**1a**	4-CHO-C_6H_4	CO_2Me	**9d**	7.80	73	20	90
5	**1a**	3-CHO-C_6H_4	CO_2Et	**9e**	7.75	76	25	80
6	**1b**	4-CHO-C_6H_4	CN	**9f**	0.75	90	7	89
7	**1c**	4-CHO-C_6H_4	CN	**9g**	2.30	75	15	85

[a] Isolated yields



(7a): R^1=H, **(7b):** R^1= Me, **(7c):** R^1= F, **(7d):** R^1= Br

Scheme 4 The synthesis of 3-amino spirobenzo[*c*]pyrano[3, 2-*a*]phenazine derivatives

Table 4 The synthesis 3-amino spirobenzo[*c*]pyrano[3, 2-*a*]phenazine derivatives via the reaction between 2-hydroxy-1,4-naphthoquinone (1 mmol), 1,2-diamine (1 mmol), isatins or acenaphthenequinone (1 mmol), and malono derivatives (1 mmol) in the presence of DABCO (0.3 mmol) in EtOH under reflux condition and microwave irradiation

Entry	Diamin	Cyclic ketone	X	Product	Conventional heating (Method A)		Microwave irradiation (Method B)	
					Time (h)	Yield[a] (%)	Time (min)	Yield[a] (%)
1	**1a**	Isatin	CN	**10a**	5.00	93	20	94
2	**1a**	5-Methyl isatin	CN	**10b**	8.00	90	25	89
3	**1a**	5-Fluoro isatin	CN	**10c**	7.60	90	25	88
4	**1a**	5-Bromo isatin	CN	**10d**	7.65	94	30	92
5	**1a**	Isatin	CO_2Me	**10e**	14.50	85	47	87
6	**1a**	Isatin	CO_2Et	**10f**	14.00	84	45	86
7	**1a**	5-Bromo isatin	CO_2Me	**10g**	15.50	87	50	87
8	**1a**	5-Bromo isatin	CO_2Et	**10h**	15.00	88	48	90
9	**1b**	Isatin	CN	**10i**	4.75	90	18	92
10	**1b**	5-Methyl isatin	CN	**10j**	6.75	85	25	88
11	**1c**	Isatin	CN	**10k**	7.00	82	28	84
12	**1d**	Isatin	CN	**10l**	5.50	75	20	78

[a] Isolated yields

Table 5 The condensation reaction of benzene-1,2-diamine (1a), 2-hydroxy-1,4-naphthoquinone (2) with benzaldehyde (5a) and malononitrile (4a) in the presence of recovered catalyst. (Method A)

Run	Time (min)	Yield[a] (%)
1	45	94
2	45	95
3	50	94
4	55	92
5	55	90

[a] Isolated yields

orated under reduced pressure, and the resulting solid was washed with EtOAc and was kept in refrigerator to separate DABCO as crystals. In all cycles the catalyst was recovered as stated above. The recovered catalyst was reused five times. As is shown in Table 5, no loss of catalytic activity was observed even after five cycles of the reaction.

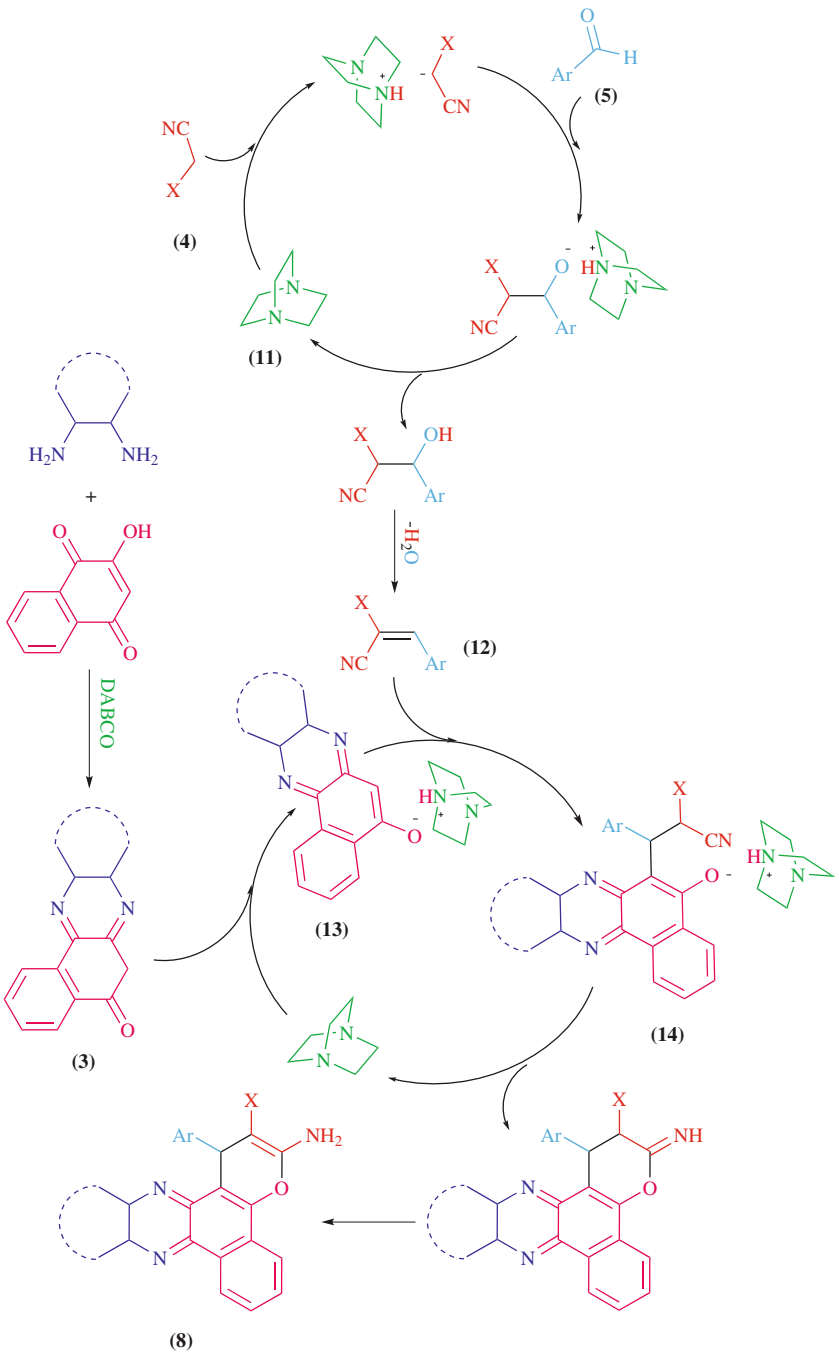
The selectivity in the synthesis of 3-amino-1*H*- benzo[*c*]pyrano[3, 2-*a*]phenazines (**6**) in the presence of DABCO (**11**) can be explained by the strict sequence of the reactions shown in Scheme 4. On the basis of this mechanism, DABCO is an effective catalyst for the formation of olefin (**12**), which readily prepares *in situ* from Knoevenagel condensation of aldehyde (**5**) with a highly reactive malono derivative (**4**). In the presence of DABCO, phenazine compound (**3**) converts to its corresponding enolate form (**13**), to be able to react easily with olefin (**12**) and to eventually give rise to the formation of intermediate (**14**), which then causes the inner molecular ring to be formed after a tautomeric proton shift to produce 3-amino-1*H*- benzo[*c*]pyrano[3, 2-*a*]phenazines (**8**) (Scheme 5).

Experimental

All chemicals were purchased from Merck, Fluka, or Aldrich Chemical Companies. All reactions were carried out using a laboratory microwave oven (MicroSYNTH, Milestone Company, Italy). The ^{1}H NMR (400 MH_z or 500MH_z) and ^{13}C NMR (100 MHz or 125 MH_z) were recorded on a BrukerAvance DPX-250, FT-NMR spectrometer (δ in ppm). Tetramethylsailane (TMS) was used as internal standard. Microanalysis was performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes and are uncorrected.

General procedure for the synthesis of benzo[*c*]pyrano[3,2-*a*]phenazine derivatives using the conventional heating method (Method A)

At first, 2-hydroxy-1,4-naphthoquinone (1 mmol) and 1,2-diamine (1 mmol) were added to a 25-mL round-bottomed flask containing DABCO (0.3 mmol) in ethanol (10 mL). The flask was fitted with a condenser, and the resulting mixture was heated to reflux under stirring. After the required time for the formation of corresponding phenazine (2–10 h), carbonyl compound (1 mmol), and alkylmalonate derivative (1 mmol) were added into the reaction mixture. Upon completion of the reaction (monitored by TLC), the reaction mixture was allowed to cool to room temperature. The solid



Scheme 5 The proposed mechanism for the synthesis of benzo[*c*]pyrano[3, 2-*a*]phenazine in the presence of DABCO

product was filtered, dried, and subsequently recrystallized from hot ethanol.

General procedure for the synthesis of benzo[*c*]pyrano[3,2-*a*]phenazine derivatives using the microwave heating method (Method B)

Synthetic pathway for the benzo[*c*]pyrano[3, 2-*a*]phenazine derivatives using the microwave heating method requires two steps. First, 2-hydroxy-1,4-naphthoquinone (1 mmol) and 1,2-diamine (1 mmol) were added to a 25 mL round-bottomed flask containing DABCO (0.3 mmol) in ethanol (10 mL) that was connected to a condenser, and the resulting mixture was heated to reflux under stirring until the formation of corresponding phenazine (2–10 h) (step 1). Then, this mixture was transferred to a microwave vessel containing carbonyl compound (1 mmol) and alkylmalonate derivatives (1 mmol) and then microwave irradiated in a multistep mode with interval (30 s–40 s–30 s) in 80 °C and 200 W irradiation (step 2). Upon completion of the reaction, monitored by TLC, the reaction mixture was allowed to cool to room temperature. The solid product was filtered, dried,

and subsequently recrystallized from hot ethanol for more purification.

Selected spectral data of the products

*3-Amino-1-phenyl-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (**8a**)*

Method A (0.380 g, 95 %), Method B (0.368 g, 92 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3457, 3315, 3168, 2193, 1350, 1270 cm^{-1}. ^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 5.37 (s, 1H, CH), 7.08 (t, J = 7.4 Hz, 1H, H–Ar), 7.21 (t, J = 7.6 Hz, 2H, H–Ar), 7.36–7.38 (m, 4H), 7.85–7.86 (m, 3H), 7.86 (t, J = 4.8 Hz, 1H, H–Ar), 8.00–8.12 (m, 1H, H–Ar), 8.13–8.15 (m, 1H, H–Ar), 8.36 (d, J = 8.0 Hz, 1H, H–Ar), 9.06 (d, J = 8.0 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 37.8, 58.5, 114.2, 120.7, 122.4, 125.1, 125.9, 126.9, 128.1, 129.0, 129.3, 129.4, 130.3, 130.5, 130.8, 131.0, 140.0, 140.3, 140.9, 141.8, 145.7, 146.5, 160.2, 160.3. Anal. Calcd. for $C_{26}H_{16}N_4O$: C, 77.99; H, 4.03; N, 13.99 %. Found: C, 76.28; H, 4.19; N, 13.57 %.

*3-Amino-1-(4-fluorophenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (**8b**)*

Method A (0.397 g, 95 %), Method B (0.376 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3449, 3310, 3170, 2187, 1330, 1280 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.36 (s, 1H, CH), 7.035 (t, J = 8.8 Hz, 2H, H–Ar), 7.38–7.41 (m, 4H, H–Ar and NH_2), 7.84–7.91 (m, 3H, H–Ar), 7.93 (t, J = 7.4 Hz, 1H, H–Ar), 8.01 (t, J = 4.6 Hz, 1H, H–Ar), 8.14 (t, J = 4.8 Hz, 1H, H–Ar), 8.35 (d, J = 7.6 Hz, 1H, H–Ar), 9.06 (d, J = 7.6 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 37.1, 58.3, 113.8, 115.5, 120.7, 122.5, 125.1, 125.9, 129.0, 129.4, 129.9, 130.0, 130.3, 130.8, 131.0, 140.0, 140.3, 140.8, 141.8, 141.9, 146.4, 160.0, 160.1, 162.4. Anal. Calcd. for $C_{26}H_{15}FN_4O$: C, 74.63; H, 3.61; N, 13.39 %. Found: C, 74.45; H, 3.54; N, 13.43 %.

*Ethyl 3-amino-1-(3-nitrophenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carboxylate (**8c**)*

Method A (0.443 g, 90 %), Method B (0.433 g, 88 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3440, 3308, 3165, 3063, 2868, 1710, 1300, 1270, 1232 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.21 (t, J = 7.0 Hz, 3H, CH_3), 4.11 (q, J = 7.0 Hz, 2H, CH_2), 5.87 (s, 1H, CH), 7.44 (t, J = 8.0 Hz, 1H, H–Ar), 7.80–7.95 (m, 6H, H–Ar and NH_2), 7.98 (d, J = 6.8 Hz, 2H, H–Ar), 8.12 (d, J = 8.0 Hz, 1H, H–Ar), 8.17 (d, J = 8.0 Hz, 1H, H–Ar), 8.34 (s, 1H, H–Ar), 8.49 (d, J = 8.0 Hz, 1H, H–Ar), 9.11 (d, J = 8.0 Hz, 1H, H–Ar). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 14.8, 36.1, 59.5, 77.0, 115.3, 121.4, 122.7, 123.6, 125.2, 126.0, 129.0, 129.5, 129.7, 130.52, 130.59, 130.9, 131.2, 135.4, 140.2, 140.4, 141.0, 141.8, 146.6, 147.6, 149.5, 160.5, 160.5, 168.2. Anal. Calcd. for $C_{28}H_{20}N_4O_5$: C, 68.29; H, 4.09; N, 11.38 %. Found: C, 65.98; H, 3.98; N, 11.05 %.

*Methyl 3-amino-1-(3-bromophenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carboxylate (**8d**)*

Method A (0.455 g, 89 %), Method B (0.460 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3450, 3310, 3173, 2978, 1695, 1355, 1298, 1265, cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):3.68 (s, 3H, CH_3), 5.92 (s, 1H, CH), 7.14 (t, J = 7.8 Hz, 1H, H–Ar), 7.23 (d, J = 7.6 Hz, 1H, H–Ar), 7.48 (d, J = 7.6 Hz, 1H, H–Ar), 7.65 (s, 1H, H–Ar), 7.91–8.10 (m, 6H, H–Ar and NH_2), 8.31–8.34 (m, 2H, H–Ar), 8.56 (d, J = 8 Hz, 1H, H–Ar), 9.28 (d, J = 8.0 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 35.5, 51.2, 77.3, 116.5, 121.5, 122.7, 125.4, 126.2, 127.5, 129.2, 129.3, 129.5, 129.6, 130.4, 130.7, 130.8, 131.0, 131.2, 131.4, 140.4, 140.6, 141.2, 142.1, 146.8, 149.8, 160.9, 168.6. Anal. Calcd. for $C_{27}H_{18}BrN_3O_3$: C, 63.29; H, 3.54; N, 8.20 %. Found: C, 62.17; H, 3.68; N, 8.35 %.

*Ethyl 3-amino-1-(4-chlorophenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carboxylate (**8e**)*

Method A (0.437 g, 91 %), Method B (0.437 g, 91 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3425, 3320, 3160, 2995, 2884, 1714, 1327, 1280, 1225 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.24 (t, J = 6.8 Hz, 3H, CH_3), 4.13 (q, J = 6.8 Hz, 2H, CH_2), 5.85 (s, 1H, CH), 7.21 (d, J = 7.6 Hz, 2H, H–Ar), 7.47 (d, J = 8.0 Hz, 2H, H–Ar), 7.90–8.03(m, 6H, H–Ar and NH_2), 8.26 (t, J = 9.0 Hz, 2H, H–Ar), 8.53 (d, J = 7.6 Hz, 1H, H–Ar), 9.22 (d, J = 7.6 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO − d_6) δ (ppm): 14.95, 35.36, 59.47, 77.70, 116.54, 122.69, 125.38, 126.22, 128.16, 129.28, 129.45, 129.60, 130.44, 130.58, 130.68, 130.74, 131.00, 131.25, 140.38, 140.54, 141.34, 142.08, 146.31, 146.63, 160.66, 168.41. Anal. Calcd. for $C_{28}H_{20}ClN_3O_3$: C, 69.78; H, 4.18; N, 8.72 %. Found: C, 70.56; H, 4.11; N, 8.73 %.

*3-Amino-1-(4-(trifluoromethyl)phenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (**8f**)*

Method A (0.439 g, 94 %), Method B (0.444 g, 95 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3440, 3305, 3150, 2196, 1374, 1290 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.62 (s, 1H, CH), 7.50 (s, 2H, NH_2), 7.60–7.67 (m,

4H), 7.95–8.02 (m, 4H), 8.04 (t, J = 7.6 Hz, 1H, H–Ar), 8.15 (d, J = 6 Hz, 1H, H–Ar), 8.30 (t, J = 4.8 Hz, 1H, H–Ar), 9.26 (d, J = 7.6 Hz, 1H, H–Ar). Anal. Calcd. for $C_{27}H_{15}F_3N_4O$: C, 69.23; H, 3.23; N, 11.96 %. Found: C, 68.14; H, 3.33; N, 11.85 %.

*3-Amino-1-(3-phenoxyphenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8g***)*

Method A (0.428 g, 87 %), Method B (0.442 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3413, 3325, 3180, 2218, 1335, 1290 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.30 (s, 1H, CH), 6.70 (dd, J = 1.6 Hz, J = 8.0 Hz, 1H, H–Ar), 6.88 (d, J = 7.6 Hz, 2H, H–Ar), 8.04-8.13 (m, 3H, H–Ar), 7.19 (t, J = 7.8 Hz, 1H, H–Ar), 7.28 (t, J = 8 Hz, 2H, H–Ar), 7.41 (s, 2H, NH_2), 7.79–7.95 (m, 5H, H–Ar), 8.13 (d, J = 3.6 Hz, 1H, H–Ar), 8.32 (d, J = 7.6 Hz, 1H, H–Ar), 9.04 (d, J = 8.0 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 37.6, 58.1, 113.8, 116.8, 118.4, 119.1, 120.7, 122.4, 122.8, 123.9, 125.1, 125.8, 129.0, 129.3, 129.4, 130.3, 130.3, 130.4, 130.5, 130.7, 131.0, 140.0, 140.4, 140.8, 141.7, 146.5, 147.9, 156.7, 156.9, 160.3. Anal. Calcd. for $C_{32}H_{20}N_4O_2$: C, 78.03; H, 4.09; N, 11.38 %. Found: C, 77.21; H, 4.12; N, 11.17 %.

*3-Amino-1-(4-(methylthio)phenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8h***)*

Method A (0.401 g, 90 %), Method B (0.388 g, 87 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3437, 3300, 3180, 2960, 2187, 1317, 1245 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.37 (s, 3H, CH_3), 5.54 (s, 1H, CH), 7.13 (d, J = 8.4 Hz, 3H, H–Ar), 7.38 (s, 1H, NH_2), 7.40 (d, J = 3.2 Hz, 2H, H–Ar), 7.95–8.10 (m, 3H, H–Ar and NH_2), 8.05 (t, J = 7.0 Hz, 1H, H–Ar), 8.24 (t, J = 4.8 Hz, 1H, H–Ar), 8.34 (t, J = 4.8 Hz, 1H, H–Ar), 8.49 (d, J = 8.4 Hz, 1H, H–Ar), 9.30 (d, J = 7.6 Hz, 1H, H–Ar). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 37.1, 45.2, 50.1, 109.2, 112.2, 114.7, 120.6, 121.4, 126.1, 126.4, 128.5, 128.7, 129.6, 129.6, 130.5, 130.9, 131.1, 133.8, 136.4, 140.2, 141.2, 151.2, 159.9, 160.5, 173.1. Anal. Calcd. for $C_{27}H_{18}N_4OS$: C, 72.63; H, 4.06; N, 12.55 %. Found: C, 72.01; H, 4.10; N, 12.33 %.

*3-Amino-1-(naphthalene-1-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8i***)*

Method A (0.400 g, 89 %), Method B (0.405 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3450, 3305, 3180, 2207, 1328, 1270 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.35 (s, 1H, CH), 7.23–7.20 (m, 2H, H–Ar), 7.34 (s, 1H, NH2), 7.39–7.51 (m, 1H, H–Ar), 7.56–7.63(m, 2H, H–Ar), 7.68 (d, J = 8.0 Hz, 1H, H–Ar), 7.79 (t, J = 7.6 Hz, 2H, H–Ar), 7.84–7.94 (m, 2H, H–Ar and NH_2), 7.98 (t, J = 7.6 Hz, 1H, H–Ar), 8.05 (t, J = 7.4 Hz, 1H, H–Ar), 8.22 (d, J = 8.4 Hz, 1H, H–Ar), 8.5 (d, J = 8 Hz, 1H, H–Ar), 8.90 (d, J = 8.4 Hz, 1H, H–Ar), 9.23 (d, J = 8 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 39.2, 59.3, 115.2, 120.6, 122.6, 124.8, 125.4, 126.1, 126.2, 126.2, 127.4, 128.1, 128.7, 128.8, 129.5, 129.6, 130.4, 130.6, 131.1, 131.3, 133.6, 134.5, 135.4, 140.2, 140.5, 141.3, 141.8, 143.6, 147.0, 160.0. Anal. Calcd. for $C_{30}H_{18}N_4O$: C, 79.98; H, 4.03; N, 12.44 %. Found: C, 80.66; H, 3.95; N, 12.18 %.

*3-Amino-1-(naphthalene-2-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8j***)*

Method A (0.405 g, 90 %), Method B (0.396 g, 88 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3453, 3303, 3177, 2210, 1348, 1250 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.60 (s, 1H, CH), 7.36–4.44 (m, 4H, H–Ar), 7.52 (dd, J = 1.2 Hz, J = 8.8 Hz, 1H, H–Ar), 7.75 (dd, J = 4.6 Hz, J = 7.75 Hz, 2H, H–Ar), 7.81–7.90 (m, 4H, H–Ar), 7.96 (s, 2H, NH_2), 8.06 (dd, J = 2.2 Hz, J = 7.3 Hz, 1H, H–Ar), 8.14 (dd, J = 2.2 Hz, J = 7.3 Hz, 1H, H–Ar), 8.43 (d, J = 8.0 Hz, 1H, H–Ar), 9.11 (d, J = 8.0 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 38.3, 58.3, 113.9, 120.7, 122.7, 125.3, 126.11, 126.14, 126.5, 126.6, 126.7, 127.8, 128.1, 128.4, 129.1, 129.51, 129.57, 130.5, 130.6, 130.9, 131.1, 132.3, 133.3, 140.2, 140.4, 141.2, 141.9, 143.1, 146.6, 160.2. Anal. Calcd. for $C_{30}H_{18}N_4O$: C, 79.98; H, 4.03; N, 12.44 %. Found: C, 78.73; H, 4.08; N, 12.23 %.

*3-Amino-1-(1H-indol-3-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8k***)*

Method A (0.263 g, 60 %), Method B (0.307 g, 70 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3480, 3438, 3315, 3205, 2213, 1390, 1250 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.84 (s, 1H, CH), 6.89–6.91 (m, 2H, H–Ar), 7.24 (d, J = 8.0 Hz, 1H, H–Ar), 7.29 (s, 2H), 7.41 (s, 1H, H–Ar), 7.56 (d, J = 8.0 Hz, 1H, H–Ar), 7.92 (t, J = 8 Hz, 3H, H–Ar), 8.01 (t, J = 7.6 Hz, 1H, H–Ar), 8.23 (t, J = 9.6 Hz, 2H, H–Ar), 8.49 (d, J = 8.0 Hz, 1H, H–Ar), 9.20 (d, J = 7.6 Hz, 1H, H–Ar), 10.87 (s, 1H, NH). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 29.6, 58.5, 112.1, 114.5, 118.5, 118.8, 118.9, 121.14, 121.16, 122.5, 124.4, 125.3, 125.9, 126.2, 129.2, 129.3, 129.5, 130.3, 130.6, 131.0, 131.1, 136.8, 140.2, 140.4, 141.5, 142.0, 146.1, 160.3. Anal. Calcd. for $C_{28}H_{17}N_5O$: C, 76.52; H, 3.90; N, 15.94 %. Found: C, 78.29; H, 4.02; N, 15.92 %.

*3-Amino-1-benzoyl-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8l***)*

Method A (0.376 g, 88 %), Method B (0.385 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3482, 3300, 3137,

2218,1693, 1360, 1298 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.20 (s, 1H, CH), 7.58 (s, 2H, NH_2), 7.63 (d, $J = 8.4$ Hz, 1H, H–Ar), 7.70 (t, $J = 7.6$ Hz, 2H, H–Ar), 7.80 (t, $J = 7.4$ Hz, 1H, H–Ar), 7.88 (t, $J = 7.4$ Hz, 1H, H–Ar), 7.94 (t, $J = 7.4$ Hz, 1H, H–Ar), 7.99–7.08 (m, 2H, H–Ar), 8.29 (d, $J = 7.6$ Hz, 2H, H–Ar), 8.33 (d, $J = 8.4$ Hz, 1H, H–Ar), 9.29 (d, $J = 7.6$ Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 38.7, 52.4, 111.6, 112.4, 114.2, 114.8, 119.9, 122.4, 125.4, 125.8, 128.51, 128.58, 129.2, 129.3, 129.4, 129.7, 129.9, 130.5, 130.8, 131.2, 131.5, 134.1, 137.0, 140.2, 140.8, 140.9, 141.8, 147.7, 161.2, 200.4. Anal. Calcd. for $C_{27}H_{16}N_4O_2$: C, 75.69; H, 3.76; N, 13.08 %. Found: C, 73.47; H, 3.61; N, 13.49 %.

*3-Amino-1-(thiophen-2-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8m***)*

Method A (0.365 g, 90 %), Method B (0.365 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3489, 3365, 3112, 2196, 1310, 1289 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.93 (s, 1H, CH), 6.86 (dd, $J = 3.6$ Hz, $J = 4.8$ Hz, 1H, H–Ar), 7.14 (d, $J = 3.2$ Hz, 1H, H–Ar), 7.26 (d, $J = 4.8$ Hz, 1H, H–Ar), 7.55 (s, 2H, NH_2), 7.97–8.05 (m, 4H, H–Ar), 8.32–8.38 (m, 2H, H–Ar), 8.45 (d, $J = 7.6$ Hz, 1H, H–Ar), 9.29 (d, $J = 7.6$ Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 32.6, 57.6, 114.5, 119.0, 120.5, 122.6, 125.2, 125.3, 125.4, 126.0, 127.2, 129.3, 129.7, 129.8, 130.4, 131.0, 131.1, 131.5, 140.4, 140.8, 141.0, 142.0, 149.5, 161.1. Anal. Calcd. for $C_{24}H_{14}N_4OS$: C, 70.92; H, 3.47; N, 13.78 %. Found: C, 68.86; H, 3.49; N, 13.39 %.

*3-Amino-1-(5-methylthiophen-2-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8n***)*

Method A (0.373 g, 89 %), Method B (0.361 g, 86 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3507, 3372, 3108, 2995, 2184, 1300, 1270 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.24 (s, 3H, CH_3), 5.81 (s, 1H, CH), 6.52 (d, $J = 2.4$ Hz, 1H, H–Ar), 6.90 (d, $J = 3.2$ Hz, 1H, H–Ar), 7.52 (s, 2H, NH_2), 7.94–8.03 (m, 4H, H–Ar), 8.29–8.36 (m, 2H, H–Ar), 8.42 (d, $J = 7.6$ Hz, 1H, H–Ar), 9.26 (d, $J = 7.2$ Hz, 1H, H–Ar). Anal. Calcd. for $C_{25}H_{16}N_4OS$: C, 71.41; H, 3.84; N, 13.32 %. Found: C, 70.86; H, 3.72; N, 13.17 %.

*3-Amino-1-(thiophen-3-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8o***)*

Method A (0.373 g, 92 %), Method B (0.369 g, 91 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3506, 3395, 3100, 2195, 1360, 1245 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.71 (s, 1H, CH), 7.12 (d, $J = 4.8$ Hz, 1H, H–Ar), 7.36 (d, $J = 6.44$ Hz, 2H, H–Ar), 7.43 (s, 2H, NH_2), 7.94–8.03 (m, 4H, H–Ar), 8.28–8.34 (m, 2H, H–Ar), 8.45 (d, $J = 8.0$ Hz, 1H, H–Ar), 9.27 (d, $J = 7.6$ Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 32.7, 57.5, 114.6, 120.8, 122.2, 122.5, 125.4, 126.2, 126.6, 127.6, 129.4, 129.5, 129.6, 130.4, 130.8, 131.0, 131.3, 140.4, 140.6, 141.2, 142.1, 146.0, 146.6, 160.9. Anal. Calcd. for $C_{24}H_{14}N_4OS$: C, 70.92; H, 3.47; N, 13.78 %. Found: C, 70.08; H, 3.40; N, 13.38 %.

*3-Amino-1-(furan-2-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8p***)*

Method A (0.335 g, 86 %), Method B (0.343 g, 88 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3410, 3295, 3150, 2210, 1325, 1297 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 5.72 (s, 1H, CH), 6.27 (d, $J = 6.0$ Hz, 2H, H–Ar), 7.44 (s, 1H, H–Ar), 7.48 (s, 2H, NH) 7.97–8.05 (m, 4H, H–Ar), 8.26 (t, $J = 5.0$ Hz, 1H, H–Ar), 8.35 (t, $J = 5.0$ Hz, 1H, H–Ar), 8.46 (d, $J = 8.0$ Hz, 1H, H–Ar), 9.30 (d, $J = 7.6$ Hz, 1H, H–Ar). Anal. Calcd. for $C_{24}H_{14}N_4O_2$: C, 73.84; H, 3.61; N, 14.35 %. Found: C, 73.12; H, 3.56; N, 14.35 %.

*3-Amino-1-(5-methylfuran-2-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8q***)*

Method A (0.367 g, 91 %), Method B (0.363 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3450, 3315, 3190, 2895, 2208, 1290, 1265 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.10 (s, 3H, CH_3), 5.65 (s, 1H, CH), 5.86 (d, $J = 2.0$ Hz, 1H, H–Ar), 6.12 (d, $J = 3.2$ Hz, 1H, H–Ar), 7.44 (s, 2H, NH_2), 7.97–8.05 (m, 4H, H–Ar), 8.27 (t, $J = 5.0$ Hz, 1H, H–Ar), 8.35 (t, $J = 5.0$ Hz, 1H, H–Ar), 8.46 (d, $J = 7.6$ Hz, 1H, H–Ar), 9.30 (d, $J = 7.2$ Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 13.8, 25.0, 78.4, 105.1, 107.2, 116.5, 117.9, 121.7, 122.3, 128.8, 129.2, 129.4, 129.6, 130.2, 130.5, 130.8, 131.4, 132.0, 140.1, 140.3, 141.6, 146.4, 148.0, 157.3, 157.5. Anal. Calcd. for $C_{25}H_{16}N_4O_2$: C, 74.25; H, 3.99; N, 13.85 %. Found: C, 72.36; H, 4.13; N, 13.30 %.

*3-Amino-1-(1H-pyrrol-2-yl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8r***)*

Method A (0.194 g, 50 %), Method B (0.233 g, 60 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3470, 3428, 3355, 3205, 2214, 1365, 1245 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.65 (s, 1H, CH), 7.21 (s, 1H), 7.84–7.93 (m, 7H, H–Ar and NH_2), 8.17 (d, $J = 8.4$ Hz, 1H, H–Ar), 8.30 (d, $J = 8.0$ Hz, 1H, H–Ar), 8.33 (dd, $J = 3.6$ Hz, $J = 7.2$ Hz, 1H, H–Ar), 9.28 (t, $J = 4.8$ Hz, 2H, H–Ar), 11.52 (s, 1H). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 30.8, 47.8, 103.9, 105.6, 107.7, 117.2, 122.6, 123.3, 125.2, 128.6, 128.9, 129.2, 129.4, 129.5, 129.7, 130.5, 130.6, 131.4, 134.8, 139.7, 139.9,

143.0, 145.7, 157.4. Anal. Calcd. for $C_{24}H_{15}N_5O$: C, 74.02; H, 3.88; N, 17.98 %. Found: C, 73.48; H, 3.85; N, 17.24 %.

*3-Amino-1-(2-nitrophenyl)-1H-benzo[f]pyrano[2,3-h]pyrido[3,2-b]quinoxaline-2-carbonitrile (***8s***)*

Method A (0.325 g, 73 %), Method B (0.347 g, 78 %). Mahogany powder, m.p. >250 °C. IR (KBr) ν_{max} 3505, 3410, 3130, 2212, 1295, 1257 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.12 (s, 1H, CH), 7.32–7.38 (m, 1H, H–Ar), 7.47–7.52 (m, 2H, H–Ar), 7.57 (s, 1H, NH_2), 7.89 (d, J = 8.0 Hz, 1H, H–Ar), 7.94–7.99 (m, 3H, H–Ar and NH_2), 8.04 (t, J = 7.6 Hz, 1H, H–Ar), 8.35 (dd, J = 1.6 Hz, J = 8.4 Hz, 1H, H–Ar), 8.48 (t, J = 6.2 Hz, 1H, H–Ar), 9.15 (d, J = 8.0 Hz, 1H, H–Ar), 9.27 (t, J = 1.8 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 32.2, 56.8, 113.0, 119.7, 122.9, 124.0, 125.8, 126.3, 126.7, 128.4, 130.1, 130.5, 131.3, 131.7, 134.0, 137.2, 137.6, 140.1, 141.6, 142.2, 147.1, 148.2, 149.9, 155.8, 160.5. Anal. Calcd. for $C_{25}H_{14}N_6O_3$: C, 67.26; H, 3.16; N, 18.83 %. Found: C, 67.02; H, 3.10; N, 19.11 %.

*3-Amino-11-nitro-1-(4-nitrophenyl)-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile, (***8t***)*

Method A (0.294 g, 60 %), Method B (0.308 g, 63 %). Orange powder, m.p. >250 °C. IR (KBr) ν_{max} 3443, 3368, 3126, 2207, 1305, 1225 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.32 (s, 1H, CH), 7,51 (s, 2H, NH_2), 7.64 (d, J = 8.8 Hz, 2H, H–Ar), 7.89 (t, J = 7.6 Hz, 1H, H–Ar), 7.95 (t, J = 6.6 Hz, 1H, H–Ar), 8.04 (d, J = 9.2 Hz, 1H, H–Ar), 8.12 (d, J = 8.8 Hz, 2H, H–Ar), 8.26 (d, J = 8.0 Hz, 1H, H–Ar), 8.40 (dd, J = 2.4 Hz, J = 9.2 Hz, 1H, H–Ar), 8.64 (dd, J = 2.0 Hz, J = 13.2 Hz, 1H, H–Ar), 8.87 (d, J = 7.6 Hz, 1H, H–Ar). Anal. Calcd. for $C_{26}H_{14}N_6O_5$: 49C, 63.67; H, 2.88; N, 17.14 %. Found: C, 61.49; H, 3.01; N, 17.31 %.

*3-Amino-1-(3-chlorophenyl)-9a,10,11,12,13,13a-hexahydro-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile (***8u***)*

Method A (0.220 g, 50 %), Method B (0.250 g, 57 %). Dun powder, m.p. >250 °C. IR (KBr) ν_{max} 3513, 3385, 3148, 2945, 2220, 1318, 1245 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.87–2.10 (m, 4H), 2.84–2.94 (m, 3H), 3.064–3.20 (m, 3H), 5.39 (s, 1H, CH), 7.20 (d, J = 7.2 Hz, 1H, H–Ar), 7.26 (d, J = 7.2 Hz, 2H, H–Ar), 7.34 (s, 1H, H–Ar), 7.40 (s, 2H, NH_2), 7.83 (t, J = 7.4 Hz, 1H, H–Ar), 7.89 (t, J = 7.2 Hz, 1H, H–Ar), 8.39 (d, J = 8.0 Hz, 1H, H–Ar), 8.97 (d, J = 8.0 Hz, 1H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 22.4, 22.6, 32.6, 37.7, 57.4, 86.6, 113.8, 120.6, 122.0, 124.2, 124.5, 126.8, 127.0, 128.0, 128.8, 129.4, 130.3, 130.7, 133.2, 136.5, 137.4, 144.6, 148.3, 151.7, 153.5, 160.7. Anal. Calcd. for $C_{26}H_{21}ClN_4O$: C, 70.82; H, 4.80; N, 12.71 %. Found: C, 69.18; H, 4.97; N, 12.69 %.

*1,1′-(1,4-Phenylene)bis(3-amino-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile) (***9a***)*

Method A (0.642 g, 89 %), Method B (0.664 g, 92 %). Yellow powder, m.p. >300 °C. IR (KBr) ν_{max} 3485, 3370, 3198, 2194, 1347, 1235 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.43 (s, 2H, 2 × CH), 7.09 (d, J = 4.0 Hz, 2H, H–Ar), 7.32 (s, 2H, NH_2), 7.68 (d, J = 8.4 Hz, 2H, H–Ar), 7.80 (t, J = 7.6 Hz, 2H, H–Ar), 7.36–7.97 (m, 2H, H–Ar), 8.04–8.15 (m, 2H, H–Ar), 8.19 (s, 2H, NH_2), 8.28 (d, J = 8.0 Hz, 2H, H–Ar), 8.37 (d, J = 7.2 Hz, 2H, H–Ar), 8.49 (d, J = 7.6 Hz, 2H, H–Ar), 9.20 (d, J = 7.6 Hz, 2H, H–Ar), 9.28 (d, J = 6.8 Hz, 2H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 38.6, 60.7, 107.5, 118.1, 122.6, 124.6, 125.4, 125.9, 129.1, 127.3, 129.5, 129.6, 130.3, 130.9, 131.1, 140.1, 140.3, 140.4, 141.8, 145.7, 151.2, 157.6, 162.8. Anal. Calcd. for $C_{46}H_{26}N_8O_2$: C, 76.44; H, 3.63; N, 15.50 %. Found: C, 76.15; H, 3.81; N, 14.84 %.

*1,1′-(1,3-Phenylene)bis(3-amino-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile) (***9b***)*

Method A (0.635 g, 88 %), Method B (0.650 g, 90 %). Yellow powder, m.p. >300 °C. IR (KBr) ν_{max} 3398, 3356, 3124, 2216, 1318, 1257 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 5.41 (s, 2H, 2 × CH), 7.08 (s, 1H, H–Ar), 7.31 (s, 2H, NH_2), 7.67 (d, J = 8.4 Hz, 2H, H–Ar), 7.79 (t, J = 7.6 Hz, 4H, H–Ar), 7.84–8.03 (m, 5H, H–Ar), 8.26 (d, J = 8.4 Hz, 2H, H–Ar), 8.36 (d, J = 7.6 Hz, 2H, H–Ar), 8.48 (s, 2H, NH_2), 9.18 (d, J = 8.0 Hz, 2H, H–Ar), 9.26 (d, J = 7.6 Hz, 2H, H–Ar). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 37.6, 61.5, 114.5, 119.8, 122.4, 125.3, 125.4, 126.7, 128.7, 128.8, 129.4, 129.5, 129.5, 129.6, 130.5, 130.7, 131.1, 140.1, 140.3, 145.6, 146.8, 152.7, 157.1, 160.3. Anal. Calcd. for $C_{46}H_{26}N_8O_2$: C, 76.44; H, 3.63; N, 15.50 %. Found: C, 77.38; H, 3.49; N, 15.17 %.

*Diethyl 1,1′-(1,4-phenylene)bis(3-amino-1H-benzo[c]pyrano[3,2-a]phenazine-2-carboxylate) (***9c***)*

Method A (0.612 g, 75 %), Method B (0.718 g, 88 %). Yellow powder, m.p. >300 °C. IR (KBr) ν_{max} 3440, 3370, 3120, 3050, 2985, 1720, 1685, 1317, 1263, 1245, 1210 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 1.28 (t, J = 7.0 Hz, 6H, 2 × CH_3), 4.28 (q, J = 7.2 Hz, 4H, 2 × CH_2), 5.93 (s, 2H, 2 × CH), 7.39–7.57 (m, 4H, H–Ar), 7.58 (d, J = 7.6 Hz, 2H, H–Ar), 7.66 (d, J = 8.0 Hz, 2H, H–Ar), 7.74 (d, J = 8.0 Hz, 2H, H–Ar), 7.84 (d, J = 7.6 Hz, 2H, H–Ar), 8.27 (s, 2H, NH_2), 8.3 (s, 2H, NH_2), 8.52 (t, J = 6.8 Hz, 4H, H–Ar), 9.16 (d, J = 8.0 Hz, 4H, H–Ar). ^{13}CNMR

(100 MHz, DMSO-d_6) δ (ppm): 14.9, 35.8, 59.4, 77.6, 116.3, 122.5, 125.8, 127.9, 128.3, 128.9, 128.9, 129.2, 130.4, 130.6, 131.2, 135.1, 139.6, 140.4, 140.4, 141.1, 141.3, 141.9, 148.6, 155.6, 160.7, 168.4. Anal. Calcd. for $C_{50}H_{36}N_6O_6$: C, 73.52; H, 4.44; N, 10.29 %. Found: C, 70.76; H, 4.27; N, 10.53 %.

*Dimethyl 1,1′-(1,4-phenylene)bis(3-amino-1H-benzo[c]pyrano[3,2-a]phenazine-2-carboxylate) (**9d**)*

Method A (0.575 g, 73 %), Method B (0.709 g, 90 %). Yellow powder, m.p. >300 °C. IR (KBr) ν_{max} 3455, 3320, 3193, 2886, 1695, 1319, 1243, 1190 cm^{-1}. Anal. Calcd for $C_{48}H_{32}N_6O_6$: C, 73.09; H, 4.09; N, 10.65 %. Found: C, 74.18; H, 4.16; N, 10.32 %.

*Diethyl 1,1′-(1,3-phenylene)bis(3-amino-1H-benzo[c]pyrano[3,2-a]phenazine-2-carboxylate) (**9e**)*

Method A (0.620 g, 76 %), Method B (0.652 g, 80 %). Yellow powder, m.p. >300 °C. IR (KBr) ν_{max} 3495, 3383, 3205,2936, 2873, 1720, 1320, 1253, 1234 cm^{-1}. Anal. Calcd for $C_{50}H_{36}N_6O_6$: C, 73.52; H, 4.44; N, 10.29 %. Found: C, 74.00; H, 4.38; N, 10.40 %.

*1,1′-(1,4-Phenylene)bis(3-amino-11,12-dimethyl-1H-benzo[c]pyrano[3,2-a]phenazine-2-carbonitrile) (**9f**)*

Method A (0.700 g, 90 %), Method B (0.692 g, 89 %). Yellow powder, m.p. >300 °C. IR (KBr) ν_{max} 3507, 3348, 3237, 2215, 1385, 1243 cm^{-1}. Anal. Calcd for $C_{50}H_{34}N_8O_2$: C, 77.10; H, 4.40; N, 14.39 %. Found: C, 75.13; H, 4.51; N, 14.33 %.

*1,1′-(1,4-Phenylene)bis(3-amino-1H-dibenzo[c,i]pyrano[3,2-a]phenazine-2-carbonitrile (**9g**)*

Method A (0.616 g, 75 %), Method B (0.698 g, 85 %). Green powder, m.p. >300 °C. IR (KBr) ν_{max} 3489, 3372, 3154, 2193, 1335, 1225 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.08 (s, 2H, 2 × CH), 7.23 (t, J = 6.2 Hz, 4H, H–Ar), 7.33 (d, J = 9.2 Hz, 2H, H–Ar), 7.40 (s, 2H, H–Ar), 7.44 (d, J = 8.0 Hz, 2H, H–Ar), 7.57 (d, J = 6.8 Hz, 2H, H–Ar), 7.72 (s, 2H, H–Ar), 7.86 (s, 2H, NH_2), 7.93–7.96 (m, 4H, H–Ar), 8.10 (d, J = 9.2 Hz, 2H, H–Ar), 8.20 (d, J = 5.2 Hz, 2H, H–Ar), 8.25 (d, J = 7.6 Hz, 2H, H–Ar), 8.80 (s, 2H, NH_2).^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 39.0, 58.4, 117.8, 119.0, 123.0, 125.0, 125.1, 125.3, 125.5, 127.0, 127.3, 127.7, 127.8, 128.1, 128.1, 128.4, 128.6, 130.6, 131.1, 131.3, 132.5, 137.5, 138.9, 141.8, 153.5, 160.4, 161.9. Anal. Calcd. for $C_{54}H_{30}N_8O_2$: C, 78.82; H, 3.67; N, 13.62 %. Found: C, 75.95; H, 3.78; N, 13.20 %.

*3-Amino-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (**10a**)*

Method A (0.410 g, 93 %), Method B (0.414 g, 94 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3510, 3340, 3298, 3170, 2226, 1650, 1308, 1215 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.75 (t, J = 7.4 Hz, 1H, H–Ar), 6.99 (d, J = 7.3 Hz, 1H, H–Ar), 7.04 (d, J = 7.7 Hz, 1H, H–Ar), 7.17 (t, J = 7.5 Hz, 1H, H–Ar), 7.53 (s, 2H, NH_2), 7.66 (m, 1H, H–Ar), 7.86–7.88 (m, 2H, H–Ar), 7.97 (t, J = 7.5 Hz, 1H, H–Ar), 8.03 (t, J = 7.4 Hz, 1H, H–Ar), 8.23 (m, 1H, H–Ar), 8.50 (d, J = 7.9 Hz, 1H, H–Ar), 9.22 (d, J = 7.8 Hz, 1H, H–Ar), 10.83 (s, 1H, NH). Anal. Calcd. for $C_{27}H_{15}N_5O_2$: C, 73.46; H, 3.42; N, 15.86 %. Found: C, 73.53; H, 3.36; N, 15.31 %.

*3-Amino-5′-methyl-2v-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (**10b**)*

Method A (0.409 g, 90 %), Method B (0.404 g, 89 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3493, 3355, 3306, 3158, 2895, 2189, 1663, 1314, 1225 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 2.02 (s, 3H, CH_3), 6.82 (s, 1H, H–Ar), 6.92 (d, J = 7.8 Hz, 1H, H–Ar), 6.96 (dd, J = 0.77 Hz, J = 7.9 Hz, 1H, H–Ar), 7.51 (s, 2H, NH_2), 7.72–7.74 (m, 1H, H–Ar), 7.87–7.89 (m, 2H, H–Ar), 7.97 (t, J = 7 Hz, 1H, H–Ar), 8.03, (t, J = 6.9 Hz, 1H, H–Ar), 8.23-8.25 (m, 1H, H–Ar), 8.50 (d, J = 7.7 Hz, 1H, H–Ar), 9.22 (d, J = 7.4 Hz, 1H, H–Ar), 10.72 (s, 1H, NH). ^{13}CNMR (125 MHz, DMSO-d_6) δ (ppm): 21.3 ($\underline{C}H_3$), 50.1, 58.3, 109.8, 111.3, 118.7, 123.3, 124.9, 125.7, 126.3, 128.8, 129.5, 129.9, 130.6, 131.1, 131.2, 131.3, 131.6, 136.6, 140.2, 140.8, 141.2, 141.2, 141.9, 148.3, 160.2, 179.9. Anal. Calcd. for $C_{28}H_{17}N_5O_2$: C, 73.84; H, 3.76; N, 15.38 %. Found: C, 70.64; H, 3.93; N, 15.06 %.

*3-Amino-5′-fluoro-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (**10c**)*

Method A (0.413 g, 90 %), Method B (0.403 g, 88 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3485, 3346, 3318, 3150, 2217, 1653, 1331, 1208 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 6.99 (d, J = 8.5 Hz, 2H, H–Ar), 7.02–7.05(m, 1H, H–Ar), 7.59 (s, 2H, NH_2), 7.68–7.70 (m, 1H, H–Ar), 7.87–7.90 (m, 2H, H–Ar), 7.99 (t, J = 7.0 Hz, 1H, H–Ar), 8.04 (t, J = 4.0 Hz, 1H, H–Ar), 8.24-8.26 (m, 1H, H–Ar), 8.50 (d, J = 7.8 Hz, 1H, H–Ar), 9.24 (d, J = 7.2 Hz, 1H, H–Ar), 10.85 (s, 1H, NH). ^{13}CNMR (125 MHz, DMSO-d_6) δ (ppm): 50.2, 57.5, 110.5, 112.2, 115.2, 118.5, 123.4, 125.7, 126.3, 128.7, 129.3, 129.9, 130.7, 131.2, 131.3, 131.6, 131.7, 132.4, 138.2, 140.3, 140.8, 141.1, 141.9, 143.2, 148.6, 160.3, 180.0. Anal. Calcd. for $C_{27}H_{14}FN_5O_2$: C, 70.58; H, 3.07; N, 15.24 %. Found: C, 71.72; H, 2.99; N, 14.85 %.

*3-Amino-5′-bromo-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (***10d***)*

Method A (0.488 g, 94 %), Method B (0.478 g, 92 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3464, 3354, 3313, 3147, 2218, 1668, 1320, 1211 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 7.02 (d, J = 8.2 Hz, 1H, H–Ar), 7.28 (s, 1H, H–Ar), 7.36 (d, J = 8.2 Hz, 1H, H–Ar), 7.61 (s, 2H, NH_2), 7.69 (dd, J = 3.2 Hz, J = 6.2 Hz, 1H, H–Ar), 7.86 (dd, J = 3.3 Hz, J = 6.2 Hz, 2H, H–Ar), 7.95 (t, J = 7.2 Hz, 1H, H–Ar), 8.02 (t, J = 7.3 Hz, 1H, H–Ar), 8.22 (dd, J = 3.2 Hz, J = 6.2 Hz, 1H, H–Ar), 8.48 (d, J = 7.8 Hz, 1H, H–Ar), 9.20 (d, J = 7.7 Hz, 1H, H–Ar), 10.98 (s, 1H, NH). ^{13}CNMR (125 MHz, DMSO-d_6) δ (ppm): 50.36, 57.43, 110.36, 112.02, 114.19, 118.56, 123.45, 125.68, 126.39, 127.36, 128.69, 129.95, 130.65, 131.19, 131.32, 131.60, 131.75, 131.95, 138.91, 140.33, 140.90, 141.12, 141.92, 143.12, 148.72, 160.42, 179.65. Anal. Calcd. for $C_{27}H_{14}BrN_5O_2$: C, 62.32; H, 2.71; N, 13.46 %. Found: C, 64.28; H, 2.62; N, 13.85 %.

*Methyl-3-amino-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carboxylate (***10e***)*

Method A (0.403 g, 85 %), Method B (0.412 g, 87 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3467, 3318, 3305, 3136, 2970, 1708, 1660, 1298, 1210 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 3.38 (s, 3H, CH_3), 6.60 (t, J = 7.0 Hz, 1H, H–Ar), 6.84 (d, J = 6.9 Hz, 1H, H–Ar), 6.94 (d, J = 7.2 Hz, 1H, H–Ar), 7.02 (t, J = 7.0 Hz, 1H, H–Ar), 7.85 (dd, J = 3.5 Hz, J = 4.7 Hz, 2H, H–Ar), 7.90–7.94 (m, 2H, H–Ar), 7.98, (t, J = 7.4 Hz, 1H, H–Ar), 8.08 (s, 1H, NH_2), 8.13 (s, 1H, NH_2), 8.20 (dd, J = 3.3 Hz, J = 4.7 Hz, 1H, H–Ar), 8.60 (d, J = 7.7 Hz, 1H, H–Ar), 9.23 (d, J = 7.7 Hz, 1H, H–Ar), 10.58 (s, 1H, NH). Anal. Calcd. for $C_{28}H_{18}N_4O_4$: C, 70.88; H, 2.57; N, 11.81 %. Found: C, 68.55; H, 2.62; N, 12.15 %.

*Ethyl-3-amino-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carboxylate (***10f***)*

Method A (0.410 g, 84 %), Method B (0.419 g, 86 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3507, 3362, 3307, 3120, 2943, 2870, 1718, 1640, 1295, 1227 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 0.94 (t, J = 7.0 Hz, 3H, CH_3), 3.86 (q, J = 6.8 Hz, 2H, CH_2), 6.62 (t, J = 7.2 Hz, 1H, H–Ar), 6.87 (d, J = 7.1 Hz, 1H, H–Ar), 6.94 (d, J = 7.6 Hz, 1H, H–Ar), 7.06 (t, J = 7.5 Hz, 1H, H–Ar), 7.82–7.92 (m, 3H, H–Ar), 7.96 (t, J = 7.3 Hz, 1H), 8.03 (t, J = 7.1 Hz, 1H, H–Ar), 8.17 (s, 2H, NH_2), 8.22, (t, J = 4.3 Hz, 1H, H–Ar), 8.60 (d, J = 7.9 Hz, 1H, H–Ar), 9.22 (d, J = 7.7 Hz, 1H, H–Ar), 10.64 (s, 1H, NH), NH.Anal. Calcd for $C_{29}H_{20}N_4O_4$: C, 71.30; H, 4.13; N, 11.47 %. Found: C, 71.05; H, 4.22; N, 10.98 %.

*Methyl-3-amino-5′-bromo-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carboxylate (***10g***)*

Method A (0.480 g, 87 %), Method B (0.481 g, 87 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3488, 3312, 3315, 3142, 2935, 1725, 1624, 1300, 1232 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 3.43 (s, 3H, CH_3), 6.93 (d, J = 8.0 Hz, 1H, H–Ar), 7.10 (s, 1H, H–Ar), 7.23 (d, J = 8.2 Hz, 1H, H–Ar), 7.86–7.90 (m, 3H, H–Ar and NH_2), 7.92 (t, J = 6.6 Hz, 1H, H–Ar), 7.97 (t, J = 7.1 Hz, 1H, H–Ar), 8.18 (t, J = 7.9 Hz, 3H, H–Ar),8.58 (d, J = 7.6 Hz, 1H, H–Ar), 9.16 (d, J = 7.0 Hz, 1H, H–Ar), 10.78 (s, 1H, NH). ^{13}CNMR (125 MHz, DMSO-d_6) δ (ppm): 50.4, 51.1, 76.6, 110.8, 112.6, 112.9, 118.8, 123.7, 125.5, 126.4, 128.7, 129.8, 130.4, 131.0, 131.1, 131.4, 131.5, 132.7, 140.0, 140.2, 140.4, 141.5, 141.7, 145.4, 147.6, 160.4, 168.5, 181.3. Anal. Calcd. for $C_{28}H_{17}BrN_4O_4$: C, 60.77; H, 3.10; N, 10.12 %. Found: C, 60.76; H, 3.00; N, 9.65 %.

*Ethyl-3-amino-5′-bromo-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carboxylate (***10h***)*

Method A (0.498 g, 88 %), Method B (0.510 g, 90 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3475, 3367, 3321, 3152, 2937, 2866, 1687, 1655, 1334, 1285 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 0.94 (t, J = 7.0 Hz, 3H, CH_3), 3.86 (q, J = 6.8 Hz, 2H, CH_2), 6.93 (d, J = 8.0 Hz, 1H, H–Ar), 7.10 (s, 1H, H–Ar), 7.23 (d, J = 8.2 Hz, 1H, H–Ar), 7.86–7.90 (m, 3H, H–Ar and NH_2), 7.92 (t, J = 6.6 Hz, 1H, H–Ar), 7.97 (t, J = 7.1 Hz, 1H, H–Ar), 8.18 (t, J = 7.9 Hz, 3H, H–Ar), 8.58 (d, J = 7.6 Hz, 1H, H–Ar), 9.16 (d, J = 7.0 Hz, 1H, H–Ar), 10.78 (s, 1H, NH). ^{13}CNMR (125 MHz, DMSO-d_6) δ (ppm): 16.2, 50.5, 54.2, 76.6, 110.8, 112.6, 112.9, 118.8, 123.7, 125.5, 126.4, 128.7, 129.8, 130.4, 131.0, 131.1, 131.4, 131.5, 132.7, 140.0, 140.2, 140.4, 141.5, 141.7, 145.4, 147.6, 160.4, 168.5, 181.3. Anal. Calcd. for $C_{29}H_{19}BrN_4O_4$: C, 61.39; H, 3.38; N, 9.87 %. Found: C, 59.07; H, 3.52; N, 9.41 %.

*3-Amino-11,12-dimethyl-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (***10i***)*

Method A (0.422 g, 90 %), Method B (0.431 g, 92 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3463, 3319, 3305, 3114, 2209, 1663, 1338, 1218 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 1.03 (s, 3H, CH_3), 3.42 (s, 3H, CH_3), 6.73 (s, 1H, H–Ar), 6.95–7.25 (m, 3H, H–Ar),7.44 (s, 1H, H–

Ar), 7.54–7.93 (m, 4H, H–Ar and NH_2), 8.14 (s, 1H, NH_2), 8.25–8.8.54 (m, 1H, H–Ar),9.12 (d, J = 16 Hz, 1H, H–Ar),10.76 (s, 1H, NH). Anal. Calcd. for $C_{29}H_{19}N_5O_2$: C, 74.19; H, 4.08; N, 14.92 %. Found: C, 74.42; H, 3.89; N, 14.96 %.

*3-Amino-5′,11,12-trimethyl-2′-oxospiro[benzo[c]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (***10j***)*

Method A (0.410 g, 85 %), Method B (0.425 g, 88 %). Yellow powder, m.p. >250 °C. IR (KBr) ν_{max} 3504, 3348, 3316, 3125, 2196, 1670, 1335, 1240 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 2.05 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 6.82 (s, 1H, H–Ar), 6.98 (s, 2H, H–Ar), 7.35–7.60 (m, 4H, H–Ar), 7.95 (s, 2H, NH_2), 8.47 (d, J = 4.4 Hz, 1H, H–Ar), 9.13 (d, J = 4.4 Hz, 1H, H–Ar), 10.97 (s, 1H, NH). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 20.5, 20.6, 20.9, 49.7, 57.9, 109.4, 111.0, 118.3, 122.8, 124.4, 125.0, 125.6, 125.9, 128.0, 129.0, 130.0, 130.8, 132.0, 136.3, 136.3, 139.0, 139.7, 140.9, 140.8, 141.8, 142.1, 147.3, 159.8, 164.0, 179.6. Anal. Calcd. for $C_{30}H_{21}N_5O_2$: C, 74.52; H, 4.38; N, 14.48 %. Found: C, 72.59; H, 4.49; N, 14.16 %.

*3-Amino-2′-oxospiro[dibenzo[c,i]pyrano[3,2-a]phenazine-1,3′-indoline]-2-carbonitrile (***10k***)*

Method A (0.402 g, 82 %), Method B (0.412 g, 84 %). Mahogany powder, m.p. >250 °C. IR (KBr) ν_{max} 3477, 3352, 33, 3170, 2226, 1650, 1336, 1241 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.80 (t, J = 7.4 Hz, 1H, H–Ar), 7.09 (d, J = 7.6 Hz, 1H, H–Ar), 7.15 (d, J = 8.0 Hz, 1H, H–Ar), 7.23 (t, J = 7.6 Hz, 1H, H–Ar), 7.10–7.68 (m, 4H, H–Ar), 7.94 (t, J = 7.4 Hz, 1H, H–Ar), 8.00 (t, J = 7.6 Hz, 1H, H–Ar), 8.10 (d, J = 5.6 Hz, 1H, H–Ar), 8.22 (t, J = 4.2 Hz, 1H, H–Ar), 8.29 (s, 1H, NH_2), 8.44 (d, J = 8.0 Hz, 1H), 8.85 (s, 1H, NH_2), 9.14 (d, J = 7.6 Hz, 1H), 10.93 (s, 1H, NH). ^{13}CNMR (100 MHz, DMSO-d_6) δ (ppm): 49.6, 57.8, 109.8, 110.7, 118.2, 123.1, 124.0, 125.5,126.9, 126.2, 127.2, 127.8, 127.8, 128.3, 128.8, 128.9, 130.4, 130.7, 131.5, 133.8, 133.9, 136.0, 137.1, 138.1, 141.1, 141.9, 143.2, 143.3, 148.5, 159.8, 179.5. Anal. Calcd. for $C_{31}H_{17}N_5O_2$: C, 75.75; H, 3.49; N, 14.25 %. Found: C, 74.10; H, 3.53; N, 14.08 %.

*3-Amino-2′-oxospiro[benzo[f]pyrano[2,3-h]pyrido[3,2-b]quinoxaline-1,3′-indoline]-2-carbonitrile (***10l***)*

Method A (0.331 g, 75 %), Method B (0.344 g, 78 %). Mahogany powder, m.p. >250 °C. IR (KBr) ν_{max} 3450, 3327, 3293, 3144, 2232, 1645, 1310, 1203 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.78 (t, J = 7.4 Hz, 1H, H–Ar), 7.05 (d, J = 7.6 Hz, 2H, H–Ar), 7.20 (t, J = 7.8 Hz, 1H, H–Ar), 7.6 (s, 2H, NH_2), 7.91 (dd, J = 4.0 Hz, J = 8.4 Hz, 1H, H–Ar), 8.01 (t, J = 7.4 Hz, 1H, H–Ar), 8.08 (d, J = 8 Hz, 2H, H–Ar), 8.52 (d, J = 8 Hz, 1H, H–Ar), 9.19-9.27 (m, 2H, H–Ar), 10.86 (s, 1H, NH). ^{13}CNMR (100 MHz, DMSO-d_6) δ(ppm): 56.5, 57.6, 109.7, 110.4, 118.1, 122.2, 123.1, 124.1, 125.9, 126.2, 126.7, 128.9, 130.5, 130.5, 131.9, 135.9, 137.1, 137.2, 141.5, 141.8, 143.2, 147.9, 148.6, 156.0, 159.8, 179.4. Anal. Calcd. for $C_{26}H_{14}N_6O_2$: C, 70.58; H, 3.19; N, 19.00 %. Found: C, 72.13; H, 3.24; N, 18.43 %.

Conclusion

In conclusion, we have reported a highly efficient and green method for the synthesis of poly-substituted 3-amino-1*H*- benzo[*c*]pyrano[3, 2-*a*]phenazines, bis-3-amino-1*H*-benzo[*c*]pyrano[3, 2-*a*]phenazines, and 3-amino spirobenzo [*c*]pyrano[3, 2-*a*]phenazines via a one-pot, two-step, four-component condensation reaction using DABCO as an inexpensive, eco-friendly, highly reactive, non-toxic and reusable solid base catalyst under conventional heating or microwave irradiation. High generality and applicability of a wide range of substrates is a remarkable advantage of our reported method for the synthesis of benzo[*c*]pyrano[3, 2-*a*]phenazine derivatives, potentially important biologically active compounds. Moreover, the use of microwave irradiation as a partially renewable energy source for the direct heating of the reaction mixture and application of DABCO as a reusable and recoverable solid base catalyst in parallel with the avoidance of hazardous organic solvents marked our work a green and economically benign methodology.

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