RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 3732

Imidazole as organocatalyst for multicomponent reactions: diversity oriented synthesis of functionalized hetero- and carbocycles using *in situ*-generated benzylidenemalononitrile derivatives†

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Received 20th September 2013
Accepted 23rd October 2013

DOI: 10.1039/c3ra45252b

www.rsc.org/advances

The multicomponent reaction of malononitrile, aldehyde and a third reaction partner such as naphthol/4-hydroxycoumarine/2-hydroxynaphthoquinone/kojic acid/enolizable ketone or thiol in the presence of imidazole as an organocatalyst provides very interesting molecular diversity. In an almost neutral reaction medium, this protocol provides easy access to highly functionalized 2-amino-4*H*-chromenes, dienes and 2-amino pyridines using *in situ*-generated aryl/alkylylidenemalononitrile derivatives obtained from the reaction of aldehydes and malononitrile along with various nucleophiles under reflux conditions in ethanol. This methodology is useful for the easy access of a wide range of structurally diverse functionalized molecules having potential application in biological systems.

Introduction

Organocatalysis is one of the most promising areas in organic synthesis and it has gained considerable attention in recent times.[1] Similarly, multicomponent reactions are a popular and greener synthetic tool to access diverse molecular scaffolds.[2] Combining both concepts, organocatalysis in multicomponent reactions (MCRs) has emerged as a very useful strategy in organic synthesis.[3] The application of small organic molecules as organocatalysts in MCRs for diversity-oriented synthesis offers many advantages, *i.e.* it avoids the use of toxic metals as well as the need to maintain an inert atmosphere during the reactions, in addition to pot, step and atom economy.

Imidazole is a versatile reagent in organic synthesis. Because of its unique reactivity pattern, it is widely used in organic synthesis. The presence of aza (–N=) and amine (–NH–) functionalities in the ring makes it amphoteric and the basicity is mild due to the presence of a pyridine-like nitrogen atom in the imidazole ring. The mild catalytic nature of imidazole minimizes side product formation and improves the yield of products. The catalytic activity of this reagent has been explored by various groups. Recently, it has been used for the monoacylation of symmetrical diamines,[4] synthesis of multisubstituted 2-aminothiophenes,[5] synthesis of polysubstituted cyclohexene,[6] 3,4-dihydropyridi-2-one derivatives by three component reactions[7] *etc.*

In continuation of our research work on multicomponent reactions,[8] we were interested to explore the catalytic potential of imidazole in our multicomponent reactions for easy access to diverse and highly substituted hetero- and carbocycles. From the literature studies we realized that highly substituted pyrans/chromenes and pyridines tethered with $-NH_2$ and –CN functionality in the 2,3-position, as shown as in Fig. 1, possesses diverse pharmacological properties.[9] Considering their importance, a considerable number of methods are found in the literature for the synthesis of these molecules.[10] Most of the reported methods are based on three component reactions (3CR), using aldehyde, malononitrile and various nucleophiles in the presence of a wide range of catalysts. Although a wide range of methods exist in the literature, still better and more efficient methods that provide easy access to these functionalized molecules are sought after due to the diverse biological applications of these molecules. As an

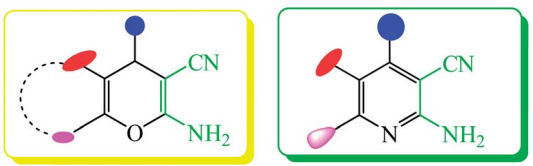

Fig. 1 Core of highly substituted 4*H*-pyran and pyridines with amino and nitrile functionality in the adjacent position having diverse pharmacological properties.

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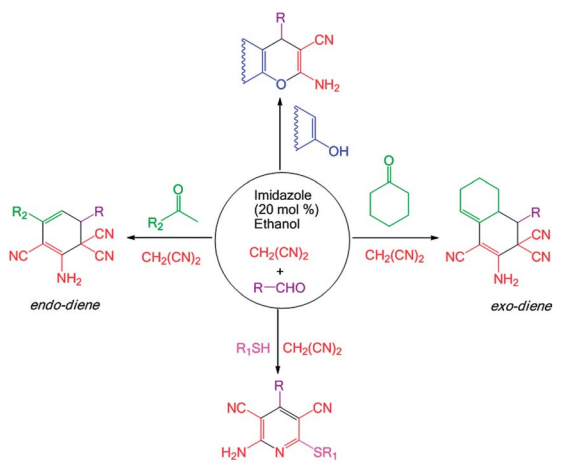
† Electronic supplementary information (ESI) available: ^1H, ^{13}C-NMR spectra of all the synthesized compounds. See DOI: 10.1039/c3ra45252b

example, recently Wang and coworkers[11] have reported the synthesis of various optically pure pyranocoumarins and 2-amino-4*H*-chromenes catalyzed by a thiourea based organocatalyst. They also investigated the antimicrobial properties of the synthesized optically pure compounds. In addition to these, some of the methods reported suffer from one drawback or another, such as the use of expensive catalysts, the need to prepare the catalyst prior to use, long reaction times, low yields and tedious procedures, or the method is limited to substrates that synthesise only one type of molecule. The necessity for the development of new methods can also be realized from the recently developed methods such as the use of potassium phthalimide-*N*-oxyl,[12] $CaCl_2$ with ultrasonic irradiation,[13] DMAP[14] *etc.*

Considering the importance of these molecules, and in continuation of our efforts towards the synthesis of functionalized heterocycles by MCRs, we wanted to explore imidazole in our MCRs, for easy access to a wide range of structurally diverse functionalized molecules using *in situ*-generated alkyl/benzylidenemalononitrile derivatives and various nucleophiles, as shown in Scheme 1.

Result and discussion

For our initial study, the reaction of 4-methoxybenzaldehyde (1.0 mmol), malononitrile (1.0 mmol) and α-naphthol (1.0 mmol) was chosen. In the absence of any catalyst and at room temperature the above reaction in ethanol provided only traces of the desired three component product **1αb** after 12 hours. Interestingly, when the same reaction was tested in the presence of 10 mol% imidazole at room temperature, the desired product was obtained in 45% yield within 12 hours. Encouraged by this result we tried to optimize the reaction conditions by varying the amount of imidazole and reaction temperature. The best result was obtained in the presence of 20 mol% of imidazole in ethanol under reflux conditions. Under these optimum reaction conditions **1αb** was obtained in 92% yield within 30 min.

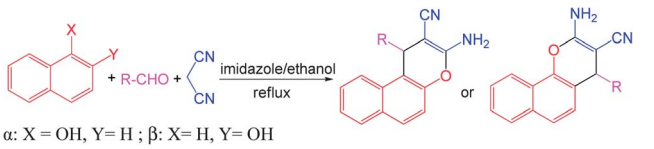


Scheme 1 Imidazole mediated MCRs for the synthesis of structurally diverse molecules.

With the optimized conditions in hand, we turned our attention to investigate the scope and general applicability of this procedure by varying the aldehyde and naphthol derivatives. Aromatic aldehydes tethered with both electron donating and withdrawing groups underwent this three component reaction smoothly under the optimized reaction conditions to afford the desired products in very good yields. Aliphatic aldehydes such as cyclohexane carboxaldehyde also underwent a similar three component reaction to provide the corresponding 2-amino-4*H*-chromene derivative **1βc** in good yield. Both α and β-naphthols are suitable for this multicomponent reaction. The results are summarized in Table 1. It is worth mentioning that, considering the importance of the 2-amino-chromenes, a wide range of methodologies for the synthesis of these compounds are being reported in the literature using various homogeneous catalysts such as DBU,[15] NaOH,[16] I_2/K_2CO_3,[17] $InCl_3$,[18] $TiCl_4$[19] *etc.* In addition to these, heterogeneous catalysts have also been used for the synthesis of 2-amino-chromenes such as nano-sized MgO,[20] nano-structured diphosphate ($Na_2CaP_2O_7$),[21] Mg/Al hydrotalcite,[22] triazine functionalized ordered mesoporous organo silica,[23] Tungstic acid functionalized mesoporous SBA-15 (ref. 24) and phosphates[25] *etc.* The present method offers a lot of advantages over most of the reported methods, such as ready availability, low cost, mild nature of the imidazole and good yields. In addition to these, the method is metal free and works under mild conditions.

Encouraged by the results of imidazole catalysis for the synthesis of 2-amino-4*H*-chromene derivatives we wanted to check whether it will also exhibit similar results in the case of other three component reactions involving the *in situ*-generated benzylidene malononitrile derivative and a nucleophile such as 2-hydroxynaphthalene-1,4-dione. Keeping the amount of imidazole 20 mol% as previously and ethanol as the solvent, the

Table 1 Imidazole mediated synthesis of 2-amino-4*H*-chromene derivatives[a]



Entry	R	α/β naphthol	Product[b]	Time (h)	Yield[c] (%)
1	C_6H_5	α	**1αa**	0.5	88
2	4-OMe–C_6H_4	α	**1αb**	0.5	92
3	4-Cl–C_6H_4	α	**1αc**	0.7	90
4	4-Br–C_6H_4	α	**1αd**	0.7	89
5	C_6H_5	β	**1βa**	1.0	86
6	4-CN–C_6H_4	β	**1βb**	1.0	93
7	C_6H_{11}	β	**1βc**	1.0	87

[a] *Reaction conditions*: aldehyde (1.0 mmol), malononitrile (1.0 mmol), α/β-naphthol (1.0 mmol), imidazole (0.2 mmol) in 5 ml ethanol under reflux conditions. [b] All products were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. [c] Isolated yield.

reaction of benzaldehyde, malononitrile and 2-hydroxynaphthalene-1,4-dione was tested under reflux conditions.

Interestingly, within 30 minutes the expected corresponding three component product **2a** was obtained in 93% yield. Similar to **2a**, **2b–2d** were also synthesized by varying the aldehydes under similar reaction conditions and the results are summarized in Table 2. It is important to mention that the purification process of all these products is very simple, as on completion of the reaction the products come out as a solid precipitate, which is filtered from the reaction mixture and the resultant solids are purified by recrystallization from ethanol.

Encouraged by these results, we attempted the present protocol for the three component reaction of kojic acid with benzylidenemalononitrile obtained from the *in situ* condensation of aromatic aldehydes and malononitrile. In this case also the reaction worked smoothly and the corresponding three component products (Table 3, entries 1–5) were obtained in good yields. Benzaldehyde derivatives such as 4-CH_3, 3-NO_2, 4-Br and 2,4-Cl-benzaldehyde underwent this three component reaction under the optimized reaction conditions and afforded the desired products (**3b–3e**) in very good yields (Table 3).

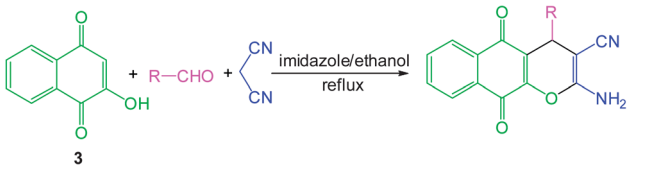
Further, to show the generality and versatility of imidazole as an organocatalyst, this protocol was extended to the synthesis of 2-amino-4-aryl/alkyl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile derivatives by a one-pot reaction of 4-hydroxycoumarin, aldehyde and malononitrile in the presence of 20 mol% imidazole and in ethanol as a solvent under reflux conditions.

Aromatic as well as aliphatic aldehydes provide the corresponding three component products in good yields (Table 4, entries 1–4).

Next we wanted to see the outcome of imidazole-mediated four component reactions of aldehyde, malononitrile and enolizable ketones. From the literature we realized that this combination (1 : 2 : 1; aldehyde : malononitrile : enolizable ketone) usually provides 2,6-dicyanoaniline derivatives in the presence of various catalysts and the substituted cyclohexa-1,3-diene intermediates are not usually isolated, due to their tendency for aromatization.[26] Recently, a few methods have been reported in the literature for the synthesis of the important diene intermediate as an exclusive product instead of 2,6-dicyano aniline. Mukhopadhyay and coworkers[27] have shown that the synthesis of 2,6-dicyanoaniline and the intermediate diene are temperature dependent. In their studies, when the reactions were performed at room temperature in water, cyclohexa-1,3-dienes were the major products, and under reflux conditions the observed products were 2,6-dicyanoanilines. Synthesis of cyclohexa-1,3-diene as a single product have also been reported using 1,2-diamine[28] at room temperature and using the ionic liquid [BMIm][BF_4][29] with reflux at 90 °C.

Interestingly, in our preliminary studies on the reaction of acetophenone (1.0 mmol) with 4-Cl-benzaldehyde (1.0 mmol)

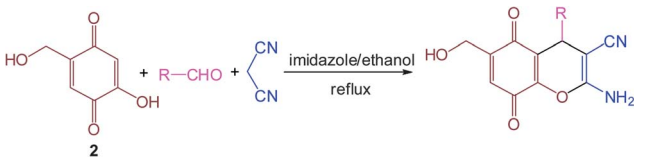
Table 2 Synthesis of 2-amino-5,10-dioxo-4-aryl/alkyl-5,10-dihydro-4*H*-benzo[*g*]chromene-3-carbonitriles[a]



Entry	R	Product[b]	Time (h)	Yield[c] (%)
1	C_6H_5	**2a**	0.5	93
2	4-OMe–C_6H_4	**2b**	0.5	92
3	4-NO_2–C_6H_4	**2c**	0.5	91
4	4-CN–C_6H_4	**2d**	0.5	94
5	C_6H_{11}	**2e**	1.0	89

[a] *Reaction conditions*: aldehyde (1.0 mmol), malononitrile (1.0 mmol), 2-hydroxynaphthalene-1,4-dione (1.0 mmol), imidazole (0.2 mmol) in 5 ml ethanol under reflux conditions. [b] All products were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. [c] Isolated yield.

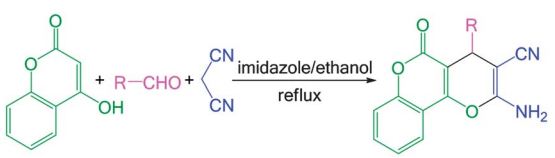
Table 3 Synthesis of 2-amino-6-(hydroxymethyl)-4-aryl/alkyl-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile[a]



Entry	R	Product[b]	Time (h)	Yield[c] (%)
1	C_6H_5	**3a**	1.5	88
2	4-Me–C_6H_4	**3b**	1.0	85
3	3-NO_2–C_6H_4	**3c**	1.0	89
4	4-Br–C_6H_4	**3d**	1.5	83
5	2,4-Cl–C_6H_3	**3e**	1.5	86

[a] *Reaction conditions*: aldehyde (1.0 mmol), malononitrile (1.0 mmol), kojic acid (1.0 mmol), imidazole (0.2 mmol) in 5 ml ethanol under reflux conditions. [b] All products were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. [c] Isolated yield.

Table 4 Synthesis of 2-amino-4-aryl/alkyl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile[a]



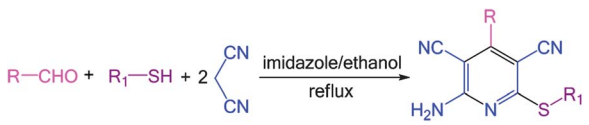
Entry	R	Product[b]	Time (h)	Yield[c] (%)
1	4-MeS–C_6H_4	**4a**	1.5	89
2	2-Naphthyl	**4b**	1.0	94
3	$C_6H_5CH_2$	**4c**	1.0	90
4	C_6H_{13}	**4d**	1.5	92

[a] *Reaction conditions*: aldehyde (1.0 mmol), malononitrile (1.0 mmol), 4-hydroxycoumarin (1.0 mmol), imidazole (0.2 mmol) in 5 ml ethanol under reflux conditions. [b] All products were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. [c] Isolated yield.

and malononitrile (2.0 mmol) in the presence of 20 mol% imidazole and ethanol as a solvent under reflux conditions, we ended up with diene **5a** as the sole product. Even after continuing the reaction for longer we did not observe any change in the reaction outcome. In a similar manner, by varying the aldehyde and ketone under the optimized reaction conditions, compound **5b** was also synthesized in good yields. Mechanistically, **5a** is the intermediate to access the corresponding 2,6-dicyano aniline derivatives. We believe that, due to the mild basicity of imidazole, the final stage elimination of HCN was not possible in this case. Thus, we realized that this imidazole mediated process may serve as an efficient tool for easy access to a wide range of functionalized dienes (carbocycles) in good yields. Interestingly, under similar reaction conditions, a cyclic ketone such as cyclohexanone provided the corresponding *exo*-cyclic diene **5c** in 81% yield instead of the *endo*-cyclic diene. Using the same procedure, **5d** was also synthesized in one pot from the reaction of cyclohexanone, malononitrile and 2-naphthaldehyde, a bulky aldehyde (Table 5).

These positive results prompted us to explore the full potential of imidazole in other MCRs involving *in situ* benzylidenemalononitrile derivatives. In continuation of our exploration of organocatalytic activity of imidazole in multicomponent reactions we turned our attention to synthesize highly substituted pyridines from the reaction of one equivalent aldehyde, two equivalents malononitrile and one equivalent thiol. Recently, we have reported a base catalyzed synthesis of highly substituted pyridines and their photo physical studies.[30] To check the suitability of imidazole for this MCR, initially the reaction of one equivalent benzaldehyde, one equivalent thiophenol and two equivalents malononitrile was tested in presence of 20 mol% imidazole under reflux conditions. Interestingly, in this case we also achieved a good result of 86% yield of **6a** within 1.0 h. Aromatic aldehydes bearing electron donating groups such as –OMe and electron withdrawing groups such as –CN were also found to be suitable in this process, with the isolated yields 91% and 90% for **6b** and **6c**, respectively. 2-Naphthaldehyde, a bulky aldehyde, showed a very good yield of 92%. An aliphatic aldehyde such as cyclohexanecarboxaldehyde was also found to be applicable in this process and gave the corresponding pyridine product **6e** with 85% isolated yield. To see the scope of the process, an aliphatic thiol such as cyclohexanethiol was also tested but in this case the reaction took a little more time as compared to the other thiols. From all these studies we have found that imidazole is a versatile organocatalyst for one pot multicomponent reactions employing *in situ*-generated alkyl/benzylidene malononitrile with various nucleophiles (Table 6).

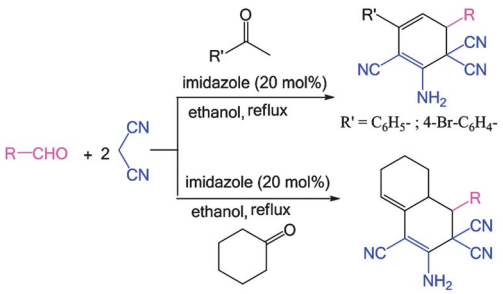
Table 6 Synthesis of 2-amino pyridine-3,5-dicarbonitrile derivatives[a]



Entry	R	R_1	Product[b]	Time (h)	Yield[c] (%)
1	C_6H_5	C_6H_5	**6a**	1.0	86
2	4-OMe–C_6H_4	C_6H_5	**6b**	0.5	91
3	4-CN–C_6H_4	2-Me–C_6H_4	**6c**	0.5	90
4	2-Naphthyl	2-Me–C_6H_4	**6d**	0.5	92
5	C_6H_{11}	C_6H_5	**6e**	1.0	85
6	4-Cl–C_6H_4	C_6H_{11}	**6f**	2.0	81

[a] *Reaction conditions*: aldehyde (1.0 mmol), malononitrile (2.0 mmol), thiol (1.0 mmol), imidazole (0.2 mmol) in 5 ml ethanol under reflux conditions. [b] All products were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. [c] Isolated yield.

Table 5 Synthesis of tetrahydronaphthalene/cyclohexa-1,3-diene[a]



Entry	Ketone	R	Product[b]	Time (h)	Yield[c] (%)
1	Acetophenone	4-Cl–C_6H_4	**5a**	9	86
2	4-Bromo acetophenone	4-OMe–C_6H_4	**5b**	12	88
3	Cyclohexanone	3-NO_2–C_6H_4	**5c**	4	81
4	Cyclohexanone	2-Naphthyl	**5d**	6	90

[a] *Reaction conditions*: aldehyde (1.0 mmol), malononitrile (2.0 mmol), enolizable ketone (1.0 mmol), imidazole (0.2 mmol) in 5 ml ethanol under reflux conditions. [b] All products were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analysis. [c] Isolated yield.

Conclusion

In summary, the present work describes imidazole-mediated multicomponent reactions involving *in situ*-generated alkyl/benzylidine malononitrile as intermediates for easy access to a wide range of highly substituted annulated pyrans, cyclohexa-1,3-dienes and 2-amino pyridines. This protocol has the advantages of a wide scope of substrates, ready availability, lower cost of the catalyst, operational simplicity, and no need for column chromatographic separation, with good to high isolated yields.

Experimental

General

All reagents were used without further purification and were procured from commercial sources. A Shimadzu FTIR spectrophotometer was used for recording IR spectra. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol 500, Varian 400 and Bruker 300/400/500 MHz spectrometers in $CDCl_3$ and DMSO-d_6 using TMS as an internal reference. Elemental analyses were carried out in a Perkin Elmer 2400 automatic CHN analyzer or Elementer Vario EL III. All compounds were characterized by their melting points, ^{1}H NMR and ^{13}C NMR spectra and elemental analysis.

General procedure for the synthesis of 2-amino-4-(aryl/alkyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (1αa–1αd and 1βa–1βc)

A mixture of aldehyde (1.0 mmol), malononitrile (1.0 mmol), imidazole (0.2 mmol) and α/β-naphthol (1.0 mmol) in 5 ml ethanol was taken in a 25 ml round bottomed flask fitted with a reflux condenser. The reaction mixture was stirred under reflux conditions. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was gradually cooled to room temperature. The solid product was collected by simple filtration and washed with ethanol and dried. The obtained solid was found to be pure enough for further characterization.

2-Amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (1αa). White solid; 88% yield; mp 222–224 °C; IR (KBr): 3446, 3349, 3252, 2963, 2854, 2214, 1649, 1597, 1519, 1468, 1391, 1270, 1184, 1031, 885, 841, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.59–7.49 (m, 3H), 7.33–7.29 (m, 2H), 7.26–7.22 (m, 3H), 7.02 (d, J = 8.4 Hz, 1H), 4.87 (s, 1H), 4.76 (bs, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 160.6, 146.2, 143.2, 133.2, 129.2, 128.1, 127.4, 127.2, 127.1, 126.7, 124.4, 123.2, 121.2, 121.0, 118.4, 56.8, 41.4 ppm; elemental analysis calc. for $C_{20}H_{14}N_2O$ (298.34): C, 80.52; H, 4.73; N, 9.39; found: C, 80.49; H, 4.71; N, 9.45%.

2-Amino-4-(4-methoxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (1αb). Light yellow solid; 92% yield; mp 191–193 °C; IR (KBr): 3428, 3339, 3246, 2957, 2868, 2213, 1641, 1592, 1521, 1460, 1393, 1268, 1181, 1032, 887, 842, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.59–7.49 (m, 3H), 7.15 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 4.83 (s, 1H), 4.75 (bs, 2H), 3.77 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 159.6, 158.5, 143.1, 137.2, 133.0, 129.0, 127.5, 126.5, 126.4, 126.1, 124.1, 123.2, 120.9, 120.4, 117.5, 114.0, 59.3, 55.1, 40.7 ppm; elemental analysis calc. for $C_{21}H_{16}N_2O_2$ (328.36): C, 76.81; H, 4.91; N, 8.53; found: C, 76.78; H, 4.94; N, 8.58%.

2-Amino-4-(4-chlorophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (1αc). White solid; 90% yield; mp 200–202 °C; IR (KBr): 3439, 3348, 3244, 2963, 2861, 2219, 1646, 1591, 1521, 1461, 1392, 1278, 1183, 1033, 883, 847, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.60–7.51 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 1H), 4.86 (s, 1H), 4.79 (bs, 2H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 159.7, 143.4, 143.3, 133.2, 132.8, 129.4, 128.8, 127.6, 126.8, 126.6, 125.9, 124.4, 123.2, 120.9, 120.2, 116.7, 58.9, 40.9 ppm; elemental analysis calc. for $C_{20}H_{13}ClN_2O$ (332.78): C, 72.18; H, 3.94; N, 8.42; found: C, 72.21; H, 3.96; N, 8.45%.

2-Amino-4-(4-bromophenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (1αd). Light yellow solid; 89% yield; mp 252–254 °C; IR (KBr): 3438, 3329, 3241, 2953, 2861, 2223, 1651, 1587, 1522, 1463, 1390, 1274, 1187, 1031, 886, 843, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.60–7.51 (m, 3H), 7.44 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 1H), 4.85 (s, 1H), 4.77 (bs, 2H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 159.9, 144.1, 143.1, 132.9, 131.4, 129.6, 127.3, 126.5, 126.3, 125.7, 123.9, 123.0, 120.9, 120.5, 120.2, 116.5, 57.4, 40.9 ppm; elemental analysis calc. for $C_{20}H_{13}BrN_2O$ (377.23): C, 63.68; H, 3.47; N, 7.43; found: C, 63.64; H, 3.50; N, 7.49%.

3-Amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (1βa). White solid; 86% yield; mp 297–299 °C; IR (KBr): 3441, 3347, 3248, 2953, 2861, 2211, 1643, 1583, 1509, 1464, 1392, 1276, 1178, 1028, 876, 847, 773 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.92 (d, J = 9.0 Hz, 1H), 7.90–7.88 (m, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.43–7.37 (m, 2H), 7.32 (d, J = 9.0 Hz, 1H), 7.25–7.21 (m, 2H), 7.18–7.16 (m, 2H), 7.12 (tt, J = 7.5, 1.5 Hz, 1H), 6.97 (bs, 2H), 5.28 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.2, 147.3, 146.2, 131.3, 130.6, 129.9, 129.2, 128.9, 127.5, 127.5, 127.1, 125.4, 124.1, 120.9, 117.3, 116.5, 58.4, 38.5 ppm; elemental analysis calc. for $C_{20}H_{14}N_2O$ (298.34): C, 80.52; H, 4.73; N, 9.39; found: C, 80.56; H, 4.78; N, 9.34%.

3-Amino-1-(4-cyanophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (1βb). Yellow-brown solid; 93% yield; mp 280–282 °C; IR (KBr): 3447, 3304, 3168, 3065, 2873, 2226, 2184, 1650, 1587, 1518, 1406, 1291, 1238, 1181, 1084, 845, 808, 735, 662, 559 cm^{-1}; ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 7.84 (d, J = 9.0 Hz, 1H), 7.82–7.79 (m, 1H), 7.63–7.61 (m, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.36–7.34 (m, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 9.3 Hz, 1H), 6.89 (bs, 2H), 5.29 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 160.0, 150.7, 147.1, 132.7, 130.9, 130.1, 129.9, 128.6, 128.0, 127.3, 125.0, 123.3, 120.4, 118.6, 116.9, 114.1, 109.9, 57.0, 38.5 ppm; elemental analysis calc. for $C_{21}H_{13}N_3O$ (323.35): C, 78.00; H, 4.05; N, 13.00; found: C, 78.04; H, 4.08; N, 13.05%.

3-Amino-1-cyclohexyl-1*H*-benzo[*f*]chromene-2-carbonitrile (1βc). White solid; 87% yield; mp 245–247 °C; IR (KBr): 3437, 3335, 3209, 3056, 2924, 2852, 2185, 1643, 1586, 1517, 1418,

1240, 1182, 1082, 967, 816, 749 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 7.87 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.54–7.51 (m, 1H), 7.42–7.39 (m, 1H), 7.16 (d, J = 8.9 Hz, 1H), 6.75 (bs, 2H), 3.98 (s, 1H), 1.82–1.56 (m, 3H), 1.54–1.38 (m, 3H), 1.17–0.94 (m, 4H), 0.90–0.78 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 162.7, 147.6, 130.7, 129.8, 128.4, 128.1, 126.8, 124.5, 122.7, 122.1, 117.3, 116.3, 51.4, 45.2, 37.7, 30.7, 26.4, 26.2, 25.8, 25.4 ppm; elemental analysis calc. for $C_{20}H_{20}N_2O$ (304.39): C, 78.92; H, 6.62; N, 9.20; found: C, 78.97; H, 6.64; N, 9.23%.

General procedure for the synthesis of 2-amino-5,10-dioxo-4-aryl/alkyl-5,10-dihydro-4*H*-benzo[*g*]chromene-3-carbonitrile (2a–2e)

The procedure for the synthesis of **2a–2e** is the same as that used for above. In this case instead of naphthol 1.0 mmol of 2-hydroxy naphthaquinone was used.

2-Amino-5,10-dioxo-4-phenyl-5,10-dihydro-4*H*-benzo[*g*]-chromene-3-carbonitrile (2a). Orange solid; 93% yield; mp 269–271 °C; IR (KBr): 3405, 3325, 3192, 3021, 2199, 1701, 1688, 1674, 1602, 1405, 1367, 1302, 1245, 1206, 1071, 1016, 948, 755, 717, 525 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 8.09–8.07 (m, 1H), 7.94–7.92 (m, 1H), 7.82–7.79 (m, 2H), 7.34–7.29 (m, 4H), 7.26–7.21 (m, 1H), 7.15 (bs, 2H), 4.67 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 182.4, 176.9, 158.6, 148.5, 143.1, 134.6, 134.0, 131.0, 130.3, 128.6, 127.6, 127.2, 126.2, 126.1, 122.8, 119.3, 57.6, 36.5 ppm; elemental analysis calc. for $C_{20}H_{12}N_2O_3$ (328.32): C, 73.16; H, 3.68; N, 8.53; found: C, 73.19; H, 3.70; N, 8.58%.

2-Amino-4-(4-methoxyphenyl)-5,10-dioxo-5,10-dihydro-4*H*-benzo[*g*]chromene-3-carbonitrile (2b). Red-brown solid; 92% yield; mp 243–245 °C; IR (KBr): 3406, 3327, 3193, 3067, 2834, 2196, 1705, 1691, 1683, 1604, 1512, 1410, 1366, 1302, 1243, 1201, 1072, 1022, 949, 835, 717, 616, 567, 530 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 8.11–8.05 (m, 1H), 7.94–7.90 (m, 1H), 7.82–7.73 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.93 (bs, 2H), 6.83 (d, J = 8.0 Hz, 2H), 4.65 (s, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 182.4, 176.9, 158.6, 158.4, 148.0, 134.9, 134.4, 133.8, 131.0, 130.1, 128.8, 126.1, 126.0, 123.1, 119.3, 113.8, 58.0, 54.9, 35.6 ppm; elemental analysis calc. for $C_{21}H_{14}N_2O_4$ (358.35): C, 70.39; H, 3.94; N, 7.82; found: C, 70.41; H, 3.97; N, 7.85%.

2-Amino-4-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-4*H*-benzo-[*g*]chromene-3-carbonitrile (2c). Orange solid; 91% yield; mp 262–264 °C; IR (KBr): 3457, 3355, 3254, 3190, 3110, 3067, 2199, 1685, 1674, 1632, 1600, 1516, 1402, 1354, 1243, 1206, 1074, 948, 862, 830, 714, 613, 532 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ = 8.15 (d, J = 9.0 Hz, 2H), 8.05–8.03 (m, 1H), 7.86–7.79 (m, 3H), 7.63 (d, J = 9.0 Hz, 2H), 7.46 (bs, 2H), 4.80 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 183.0, 177.2, 158.8, 151.5, 149.9, 147.0, 135.0, 134.7, 131.4, 131.2, 129.6, 126.6, 126.3, 124.2, 121.1, 119.5, 56.8, 36.9 ppm; elemental analysis calc. for $C_{20}H_{11}N_3O_5$ (373.32): C, 64.35; H, 2.97; N, 11.26; found: C, 64.38; H, 3.00; N, 11.30%.

2-Amino-4-(4-cyanophenyl)-5,10-dioxo-5,10-dihydro-4*H*-benzo-[*g*]chromene-3-dicarbonitrile (2d). Orange solid; 94% yield; mp 280–282 °C; IR (KBr): 3438, 3333, 3222, 3123, 3097, 3060, 2234, 2197, 1688, 1671, 1629, 1598, 1403, 1358, 1240, 1206, 1073, 1021, 945, 852, 779, 715, 615, 568 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ = 8.04–8.02 (m, 1H), 7.85–7.81 (m, 3H), 7.76 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.43 (bs, 2H), 4.72 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 183.0, 177.2, 158.8, 149.9, 149.5, 135.0, 134.7, 133.0, 131.4, 131.2, 129.3, 126.5, 126.3, 121.1, 119.5, 119.2, 110.4, 57.0, 37.1 ppm; elemental analysis calc. for $C_{20}H_{11}N_3O_3$ (341.32): C, 70.38; H, 3.25; N, 12.31; found: C, 70.35; H, 3.28; N, 12.36%.

2-Amino-4-cyclohexyl-5,10-dioxo-5,10-dihydro-4*H*-benzo[*g*]-chromene-3-carbonitrile (2e). Orange solid; 89% yield; mp 248–250 °C; IR (KBr): 3465, 3380, 3306, 3244, 3191, 2923, 2848, 2194, 1684, 1660, 1601, 1412, 1376, 1329, 1300, 1249, 1209, 1047, 944, 891, 716, 532 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ = 8.01–7.98 (m, 2H), 7.87–7.82 (m, 2H), 7.26 (bs, 2H), 3.37 (d, J = 3.0 Hz, 1H), 1.69 (d, J = 12.5 Hz, 1H), 1.62–1.54 (m, 3H), 1.49–1.42 (m, 2H), 1.32–1.25 (m, 1H), 1.16–0.99 (m, 3H), 0.92–0.81 (m, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 183.4, 177.1, 161.6, 150.5, 134.9, 134.5, 131.7, 131.1, 126.5, 126.4, 124.2, 121.3, 52.3, 44.6, 36.4, 30.8, 27.6, 26.6, 26.3, 26.0 ppm; elemental analysis calc. for $C_{20}H_{18}N_2O_3$ (334.37): C, 71.84; H, 5.43; N, 8.38; found: C, 71.86; H, 5.46; N, 8.43%.

General procedure for the synthesis of 2-amino-6-(hydroxymethyl)-4-aryl/alkyl-8-oxo-4,8-dihydropyrano [3,2-*b*]-pyran-3-carbonitrile (3a–3e)

A mixture of aldehyde (1.0 mmol), malononitrile (1.0 mmol), imidazole (0.2 mmol), kojic acid (1.0 mmol) and ethanol (5 ml) at room temperature was taken in a 25 ml round bottomed flask fitted with a reflux condenser. The reaction mixture was stirred under reflux conditions in open air. After some time the reaction mixture gave rise to a clear solution. The progress of the reaction was monitored with TLC (hexane–ethyl acetate, 7 : 3). After completion of the reaction, the reaction mixture was gradually cooled to room temperature. The solid product was collected by simple filtration, washed with ethanol and dried. The obtained solid was pure enough for further characterization.

2-Amino-6-(hydroxymethyl)-8-oxo-4-phenyl-4,8-dihydropyrano [3,2-*b*]pyran-3-carbonitrile (3a). White solid; 88% yield; 237–239 °C; IR (KBr): 3373, 3305, 3189, 3085, 3028, 2191, 1670, 1635, 1595, 1446, 1411, 1206, 1058, 1013, 852, 710, 629, 588, 528 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 7.40–7.36 (m, 2H), 7.32–7.28 (m, 3H), 7.16 (bs, 2H), 6.34 (s, 1H), 5.67 (bs, 1H), 4.72 (s, 1H), 4.23 (d, J = 15.9 Hz, 1H), 4.13 (d, J = 15.9 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 169.6, 168.1, 159.3, 148.7, 140.5, 136.3, 128.7, 127.7, 127.6, 119.1, 111.2, 59.1, 55.4, 40.5 ppm; elemental analysis calc. for $C_{16}H_{12}N_2O_4$ (296.28): C, 64.86; H, 4.08; N, 9.46; found: C, 64.89; H, 4.11; N, 9.48%.

2-Amino-6-(hydroxymethyl)-4-(4-methylphenyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (3b). Light yellow solid; 85% yield; mp 224–226 °C; IR (KBr): 3397, 3303, 3189, 3084, 3048, 2921, 2861, 2192, 1635, 1598, 1510, 1208, 1098, 1059, 1007, 861, 817, 750, 614, 521 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 7.17 (bs, 4H), 6.80 (bs, 2H), 6.40 (s, 1H), 5.80 (t, J = 6.0 Hz, 1H), 4.63 (s, 1H), 4.29 (dd, J = 16.1, 5.8 Hz,

1H), 4.19 (dd, J = 16.1, 5.8 Hz, 1H), 2.33 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 170.3, 168.4, 159.5, 149.1, 137.4, 137.2, 136.3, 129.4, 127.5, 119.2, 111.2, 59.4, 56.0, 40.3, 20.8 ppm; elemental analysis calc. for $C_{17}H_{14}N_2O_4$ (310.30): C, 65.80; H, 4.55; N, 9.03; found: C, 65.84; H, 4.57; N, 9.08%.

2-Amino-6-(hydroxymethyl)-4-(3-nitrophenyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (3c). White solid; 89% yield; mp 236–238 °C; IR (KBr): 3524, 3384, 3319, 3210, 3082, 2868, 2189, 1672, 1640, 1595, 1532, 1440, 1413, 1315, 1219, 1067, 869, 722, 551 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 8.18 (ddd, J = 8.0, 2.5, 1.0 Hz, 1H), 8.16 (t, J = 2.0 Hz, 1H), 7.80 (td, J = 8.0, 1.5 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.36 (bs, 2H), 6.33 (s, 1H), 5.65 (t, J = 6.0 Hz, 1H), 5.12 (s, 1H), 4.18 (dd, J = 15.5, 6.0 Hz, 1H), 4.11 (dd, J = 15.5, 6.0 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 170.0, 168.8, 159.9, 148.5, 148.2, 143.3, 137.1, 135.2, 131.1, 123.5, 123.0, 119.5, 112.0, 59.5, 55.2 ppm; elemental analysis calc. for $C_{16}H_{11}N_3O_6$ (341.28): C, 56.31; H, 3.25; N, 12.31; found: C, 56.33; H, 3.27; N, 12.36%.

2-Amino-4-(4-bromophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (3d). White solid; 83% yield; mp 228–230 °C; IR (KBr): 3461, 3336, 3174, 2977, 2892, 2865, 2191, 1675, 1647, 1593, 1489, 1444, 1422, 1260, 1207, 1162, 1070, 1042, 1011, 964, 877, 833, 764, 717, 689, 554, 502 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.57 (d, J = 8.5 Hz, 2H), 7.26 (bs, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.32 (s, 1H), 5.66 (t, J = 6.0 Hz, 1H), 4.83 (s, 1H), 4.19 (dd, J = 16.0, 6.0 Hz, 1H), 4.11 (dd, J = 16.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 170.0, 168.7, 159.7, 148.9, 140.7, 136.9, 132.3, 130.5, 121.6, 119.6, 111.9, 59.6, 55.7, 40.5 ppm; elemental analysis calc. for $C_{16}H_{11}BrN_2O_4$ (375.17): C, 51.22; H, 2.96; N, 7.47; found: C, 51.25; H, 2.94; N, 7.52%.

2-Amino-4-(2,4-dichlorophenyl)-6-(hydroxymethyl)-8-oxo-4,8-dihydropyrano[3,2-*b*]pyran-3-carbonitrile (3e). White solid; 86% yield; mp 258–260 °C; IR (KBr): 3446, 3342, 3196, 3067, 3026, 2974, 2889, 2190, 1676, 1641, 1595, 1562, 1474, 1441, 1412, 1384, 1316, 1208, 1164, 1049, 966, 858, 778, 682, 565 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.65 (d, J = 2.0 Hz, 1H), 7.46 (dd, J = 8.0, 1.5 Hz, 1H), 7.65 (t, J = 6.0 Hz, 1H), 7.30 (bs, 2H), 6.32 (s, 1H), 5.65 (t, J = 6.0 Hz, 1H), 5.26 (s, 1H), 4.17 (dd, J = 16.5, 6.0 Hz, 1H), 4.09 (dd, J = 15.5, 5.5 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 169.9, 168.8, 160.0, 147.9, 137.5, 137.0, 134.1, 133.9, 132.9, 129.9, 128.8, 119.3, 111.9, 59.5, 56.5, 38.2 ppm; elemental analysis calc. for $C_{16}H_{10}Cl_2N_2O_4$ (365.17): C, 52.63; H, 2.76; N, 7.67; found: C, 52.65; H, 2.74; N, 7.69%.

General procedure for the synthesis of 2-amino-4-aryl/alkyl-5-oxo-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitrile (4a–4d)

Procedure for **4a–4d** is similar to **1αa**. In these cases 4-hydroxycoumarin (1.0 mmol) was used instead of naphthol.

2-Amino-4-[4-(methylsulfanyl)phenyl]-5-oxo-4*H*,5*H*-pyrano-[3,2-*c*]chromene-3-carbonitrile (4a). White solid; 89% yield; mp 242–244 °C; IR (KBr): 3446, 3326, 3289, 3252, 3212, 3184, 2198, 1721, 1679, 1594, 1492, 1455, 1408, 1375, 1172, 1113, 1046, 954, 843, 766, 561 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.88 (d, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.49–7.43 (m, 2H), 7.38 (bs, 2H), 7.18 (bs, 4H), 4.40 (s, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.0, 158.4, 153.8, 152.6, 140.5, 137.3, 133.4, 128.8, 126.5, 125.2, 122.9, 119.7, 117.0, 113.4, 104.3, 58.3, 36.9, 15.1 ppm; elemental analysis calc. for $C_{20}H_{14}N_2O_3S$ (362.40): C, 66.28; H, 3.89; N, 7.73; found: C, 66.25; H, 3.91; N, 7.78%.

2-Amino-4-(naphthalen-2-yl)-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]-chromene-3-carbonitrile (4b). White solid; 94% yield; mp 241–243 °C; IR (KBr): 3400, 3319, 3254, 3191, 3050, 2199, 1711, 1671, 1606, 1455, 1387, 1254, 1053, 954, 905, 759 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.94–7.89 (m, 2H), 7.86–7.84 (m, 2H), 7.80 (s, 1H), 7.70 (td, J = 7.7, 1.5 Hz, 1H), 7.51–7.45 (m, 4H), 7.43 (bs, 2H), 7.39 (dd, J = 8.5, 1.5 Hz, 1H), 4.62 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.1, 158.4, 154.0, 152.7, 141.2, 133.4, 133.3, 132.7, 128.7, 128.3, 127.9, 126.7, 126.4, 126.3, 125.2, 123.0, 119.7, 117.1, 113.5, 104.2, 58.4, 37.7 ppm; elemental analysis calc. for $C_{24}H_{14}N_2O_3$ (378.38): C, 76.18; H, 3.73; N, 7.40; found: C, 76.21; H, 3.77; N, 7.44%.

2-Amino-4-benzyl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbonitrile (4c). Light yellow solid; 90% yield; mp 223–225 °C; IR (KBr): 3407, 3303, 3190, 3084, 3028, 3007, 2935, 2884, 2192, 1724, 1665, 1603, 1493, 1446, 1393, 1308, 1275, 1193, 1051, 965, 753, 713, 600, 543, 517 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.66–7.62 (m, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 8.5 Hz, 1H), 7.37–7.33 (m, 1H), 7.16 (bs, 2H), 7.14–7.08 (m, 3H), 6.91 (d, J = 7.0 Hz, 2H), 3.72 (dd, J = 8.5, 4.5 Hz, 1H), 3.05 (dd, J = 13.0, 4.5 Hz, 1H), 2.81 (dd, J = 13.0, 3.5 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.5, 159.9, 154.7, 152.4, 137.3, 133.3, 130.0, 128.3, 126.9, 125.1, 122.4, 119.9, 117.0, 113.0, 103.4, 54.8, 38.8, 33.2 ppm; elemental analysis calc. for $C_{20}H_{14}N_2O_3$ (330.34): C, 72.72; H, 4.27; N, 8.48; found: C, 72.77; H, 4.25; N, 8.52%.

2-Amino-4-hexyl-5-oxo-4*H*,5*H*-pyrano[3,2-*c*]chromene-3-carbo nitrile (4d). White solid; 92% yield; mp 228–230 °C; IR (KBr): 3403, 3326, 3253, 3195, 3060, 2915, 2869, 2854, 2204, 1713, 1678, 1609, 1455, 1394, 1315, 1208, 1185, 1108, 1042, 956, 903, 754, 526 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 7.79 (dd, J = 8.0, 1.5 Hz, 1H), 7.67 (dt, J = 8.5, 1.5 Hz, 1H), 7.45–7.42 (m, 2H), 7.27 (bs, 2H), 3.40 (dd, J = 5.5, 4.0 Hz, 1H), 1.73–1.67 (m, 1H), 1.56–1.51 (m, 1H), 1.24–1.11 (m, 8H), 0.78 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.4, 159.9, 154.6, 152.5, 133.2, 125.1, 122.6, 120.1, 117.0, 113.4, 104.7, 55.6, 34.1, 31.6, 31.3, 29.0, 24.6, 22.4, 14.3 ppm; elemental analysis calc. for $C_{19}H_{20}N_2O_3$ (324.37): C, 70.35; H, 6.21; N, 8.64; found: C, 70.39.; H, 6.25; N, 8.68%.

General procedure for the synthesis of tetrahydronaphthaalene/cyclohexa-1,3-diene (5a–5d)

A mixture of aldehyde (1.0 mmol), malononitrile (2.0 mmol), imidazole (0.2 mmol), enolizable ketone (1.0 mmol) and ethanol (5 ml) at room temperature was taken in a 25 ml round bottomed flask fitted with a reflux condenser. The reaction mixture was stirred under reflux conditions in open air. The progress of the reaction was monitored by TLC. On completion of the reaction, the reaction mixture was gradually cooled to room temperature. The solid product was collected by simple filtration and washed with ethanol and dried. The solid was further crystallized in acetonitrile to obtain pure solid.

2-Amino-6-(4-chlorophenyl)-4-phenylcyclohexa-2,4-diene-1,1,3-tricarbonitrile (5a). Yellow solid; 86% yield; mp 246–248 °C; IR (KBr): 3363, 3344, 3226, 3070, 3052, 2224, 2213, 1663, 1610, 1554, 1530, 1491, 1444, 1405, 1311, 1209, 1091, 1011, 975, 827, 772, 705, 571 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 9.13 (s, 1H), 8.97 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.56–7.46 (m, 5H + 1H), 7.31 (d, J = 5.1 Hz, 2H), 6.69 (d, J = 15.9 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 164.2, 160.7, 143.2, 135.1, 133.3, 132.7, 130.2, 129.9, 129.1, 128.5, 128.4, 125.9, 115.4, 114.70, 113.7, 102.6, 51.6 ppm; elemental analysis calc. for $C_{21}H_{13}ClN_4$ (356.81): C, 70.69; H, 3.67; N, 15.70; found: C, 70.67; H, 3.68; N, 15.67%.

2-Amino-4-(4-bromophenyl)-6-(4-methoxyphenyl) cyclohexa-2,4-diene-1,1,3-tricarbonitrile (5b). Yellow solid; 88% yield; mp 253–255 °C; IR (KBr): 3391, 3301, 3203, 3067, 3016, 2968, 2935, 2837, 2224, 2214, 1641, 1596, 1565, 1552, 1533, 1508, 1461, 1324, 1283, 1257, 1175, 1097, 1011, 976, 829, 778, 594, 539 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 9.31 (s, 1H), 9.15 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 15.6 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 15.6 Hz, 1H), 3.79 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 163.3, 161.3, 160.1, 144.5, 134.2, 132.0, 130.8, 130.3, 127.4, 123.5, 121.1, 115.8, 115.3, 114.5, 114.1, 101.5, 55.3, 52.2 ppm; elemental analysis calc. for $C_{22}H_{15}BrN_4O$ (431.28): C, 61.27; H, 3.51; N, 12.99; found: C, 61.22; H, 3.55; N, 13.04%.

2-Amino-4-(3-nitrophenyl)-5,6,7,8-tetrahydro naphthalene-1,3,3(4*H*)-tricarbonitrile (5c). White solid; 81% yield; mp 196–198 °C; IR (KBr): 3425, 3331, 3227, 3089, 3037, 3010, 2958, 2925, 2863, 2843, 2214, 1650, 1600, 1531, 1481, 1435, 1391, 1349, 1270, 1165, 1104, 910, 854, 825, 736, 723, 638, 599, 455 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.41 (s, 1H), 8.31 (d, J = 7.5 Hz, 1H), 8.09–7.81 (m, 2H), 7.39 (s, 2H), 5.76 (s, 1H), 3.94 (d, J = 12.3 Hz, 1H), 2.91 (bs, 1H), 2.23–2.07 (m, 2H), 1.67–1.46 (m, 3H), 0.89 (d, J = 12.3 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz): δ = 143.0, 138.8, 136.8, 134.1, 130.3, 128.3, 126.7, 124.0, 120.7, 116.0, 112.2, 112.0, 81.7, 49.6, 42.4, 33.5, 26.9, 24.8, 20.8 ppm; elemental analysis calc. for $C_{19}H_{15}N_5O_2$ (345.35): C, 66.08; H, 4.38; N, 20.28; found: C, 66.12; H, 4.33; N, 20.24%.

3-Amino-5,6,7,8-tetrahydro-1,2′-binaphthyl-2,2,4(1*H*)-tricarbonitrile (5d). White solid; 90% yield; mp 297–299 °C; IR (KBr): 3417, 3341, 3253, 3060, 2937, 2910, 2872, 2832, 2212, 1650, 1601, 1508, 1429, 1394, 1339, 1275, 1209, 1156, 1020, 899, 863, 825, 774, 762, 592, 481 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 8.14 (s, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.94 (m, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.56–7.52 (m, 2H), 7.30 (s, 2H), 5.78 (s, 1H), 3.60 (t, 1H), 2.93 (s, 1H), 2.20 (m, 1H), 2.10–2.03 (m, 1H), 1.65–1.47 (m, 3H), 0.95–0.89 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 143.4, 132.6, 132.2, 131.8, 130.0, 128.6, 128.3, 128.1, 127.8, 127.5, 126.7, 126.6, 123.8, 120.6, 116.0, 112.4, 81.5, 51.3, 42.7, 33.8, 26.9, 24.9, 21.0 ppm; elemental analysis calc. for $C_{23}H_{18}N_4$ (350.42): C, 78.83; H, 5.18; N, 15.99; found: C, 78.88; H, 5.13; N, 15.93%.

General procedure for the synthesis of 2-amino-4-(aryl/alkyl)-6-(aryl/alkylsulfanyl)-pyridine-3,5-dicarbonitrile (6a–6f)

A mixture of aldehyde (1.0 mmol), malononitrile (2.0 mmol), imidazole (0.2 mmol), thiol (1.0 mmol) and ethanol (5 ml) was taken in a 25 ml round bottom flask fitted with a reflux condenser. The reaction mixture was stirred under reflux conditions in open air. After some time the reaction mixture gave rise to a clear solution. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was gradually cooled to room temperature. The solid product was collected by simple filtration, washed with ethanol and dried to obtain a pure solid. The obtained solid was pure enough for further characterization.

2-Amino-4-phenyl-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile (6a). White solid; 86% yield; mp 214–216 °C. IR (KBr): 3485, 3361, 3211, 3053, 2218, 1618, 1546, 1263, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57–7.50 (m, 7H), 7.49–7.48 (m, 3H), 5.53 (bs, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 169.1, 159.3, 158.4, 135.8, 133.2, 131.0, 130.0, 129.3, 129.0, 128.5, 127.2, 115.2, 114.8, 95.9, 87.4 ppm; elemental analysis calc. for $C_{19}H_{12}N_4S$ (328.39): C, 69.49; H, 3.68; N, 17.06; found: C, 69.54; H, 3.70; N, 17.11%.

2-Amino-4-(4-methoxyphenyl)-6-(phenylsulfanyl) pyridine-3,5-dicarbonitrile (6b). White solid; 91% yield; mp 235–237 °C; IR (KBr): 3441, 3332, 3227, 3056, 2983, 2846, 2227, 2215, 1641, 1606, 1512, 1463, 1290, 1259, 1190, 1019, 837, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.55 (dd, J = 7.4, 2.3 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.48–7.45 (m, 3H), 7.05 (d, J = 8.6 Hz, 2H), 5.43 (bs, 2H), 3.87 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 166.6, 161.3, 160.2, 158.8, 135.3, 130.7, 130.1, 129.9, 127.7, 126.3, 116.0, 115.8, 114.6, 93.9, 87.5, 55.8 ppm; elemental analysis calc. for $C_{20}H_{14}N_4OS$ (358.42): C, 67.02; H, 3.94; N, 15.63%. Found: C, 67.06; H, 3.99; N, 15.68%.

2-Amino-4-(4-cyanophenyl)-6-[(2-methylphenyl)sulfanyl]-pyridine-3,5-dicarbonitrile (6c). White solid; 90% yield; mp 268–270 °C; IR (KBr): 3432, 3323, 3227, 3091, 3057, 2985, 2930, 2236, 2212, 1637, 1542, 1464, 1263, 1028, 846, 814, 755, 708 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ = 8.04–8.02 (d, J = 8.3 Hz, 2H), 7.76–7.74 (d, J = 8.3 Hz, 2H), 7.76 (bs, 2H), 7.55–7.53 (d, J = 7.56 Hz, 1H), 7.42–7.40 (m, 2H), 7.30–7.25 (m, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 166.5, 159.5, 156.6, 142.8, 138.3, 136.1, 132.5, 130.8, 130.4, 129.5, 126.7, 126.2, 117.9, 114.6, 113.3, 92.8, 86.4, 20.5 ppm; elemental analysis calc. for $C_{21}H_{13}N_5S$ (367.43): C, 68.65; H, 3.57; N, 19.06%. Found: C, 68.60; H, 3.53; N, 19.03%.

2-Amino-6-[(2-methylphenyl)sulfanyl]-4-(naphthalen-2-yl)-pyridine-3,5-dicarbonitrile (6d). White solid; 92% yield; mp 229–231 °C; IR (KBr): 3328, 3223, 3051, 2924, 2854, 2214, 1627, 1550, 1264, 1032, 761 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6, 400 MHz): δ = 8.06–8.03 (m, 2H), 8.00–7.95 (m, 2H), 7.63–7.57 (m, 3H), 7.54 (d, J = 7.5 Hz, 1H), 7.41–7.37 (m, 4H), 7.28–7.24 (m, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$ + DMSO-d_6, 100 MHz): δ = 166.7, 159.6, 158.0, 142.9, 136.1, 133.3, 132.2, 131.1, 130.6, 130.2, 128.3, 128.2, 127.5, 127.4, 126.8, 126.5, 126.4, 125.1, 115.1, 115.0, 93.6, 86.8, 20.5 ppm; elemental analysis calc. for $C_{24}H_{16}N_4S$ (392.48): C, 73.45; H, 4.11; N, 14.28%. Found: C, 73.41; H, 4.08; N, 14.24%.

2-Amino-4-cyclohexyl-6-(phenylsulfanyl)pyridine-3,5-dicarbonitrile (6e). White solid; 85% yield; mp 202–204 °C; IR (KBr): 3478, 3348, 3216, 3064, 2934, 2855, 2219, 1625, 1555, 1524, 1442, 1255, 1108, 936, 754, 706 cm^{-1}; ^1H NMR ($CDCl_3$, 300

MHz): δ = 7.53–7.50 (m, 2H), 7.45–7.39 (m, 3H), 5.41 (bs, 2H), 3.10–3.01 (m, 1H), 2.18–2.02 (m, 2H), 1.97–1.85 (m, 2H), 1.82–1.72 (m, 3H), 1.49–1.33 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.4, 164.7, 160.1, 135.9, 123.0, 129.43, 127.5, 115.7, 115.2, 95.5, 86.6, 44.8, 30.1, 26.5, 25.4 ppm; elemental analysis calc. for $C_{19}H_{18}N_4S$ (334.44): C, 68.23; H, 5.42; N, 16.75; found: C, 68.26; H, 5.47; N, 16.80%.

2-Amino-4-(4-chlorophenyl)-6-(cyclohexylsulfanyl) pyridine-3,5-dicarbonitrile (6f). White solid; 81% yield; mp 222–224 °C; IR (KBr): 3497, 3392, 3063, 2933, 2853, 2217, 1605, 1544, 1494, 1449, 1267, 1093, 835, 803, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.52 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 5.67 (bs, 2H), 3.97–3.89 (m, 1H), 2.08–2.04 (m, 2H), 1.82–1.78 (m, 2H), 1.66–1.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.9, 159.4, 156.9, 137.4, 131.9, 130.0, 129.6, 115.5, 115.0, 96.7, 86.2, 44.2, 32.8, 26.0, 25.7 ppm; elemental analysis calc. for $C_{19}H_{17}ClN_4S$ (368.88): C, 61.86; H, 4.65; N, 15.19%. Found: C, 61.81; H, 4.68; N, 15.23%.

Acknowledgements

Authors are grateful to the Department of Science and Technology, India for the financial support with Sanction no. SR/FT/CS-042/2009 and IIT Patna for carrying out this work. M. N. K. and S. K. are thankful to CSIR for their research fellowship. S. P. is grateful to UGC for his research fellowship. We are also grateful to SAIF CDRI Lucknow, Bose Institute, Kolkata, IIT Guwahati, IIT Kanpur and SAIF Panjab University for providing analytical facilities.

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