

Aliquat 336 catalysed three-component condensation in an aqueous media: A synthesis of 1*H*- and 4*H*-benzochromenes

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The synthesis, under microwave irradiation, of a series of polyfunctionalised 1*H*- and 4*H*-chromenes in water in the presence of tricaprylmethylammonium bromide (Aliquat 336) as the catalyst is reported. This method has the advantages of high yields, neutral and inexpensive medium, simple work-up procedure and environmental friendliness.

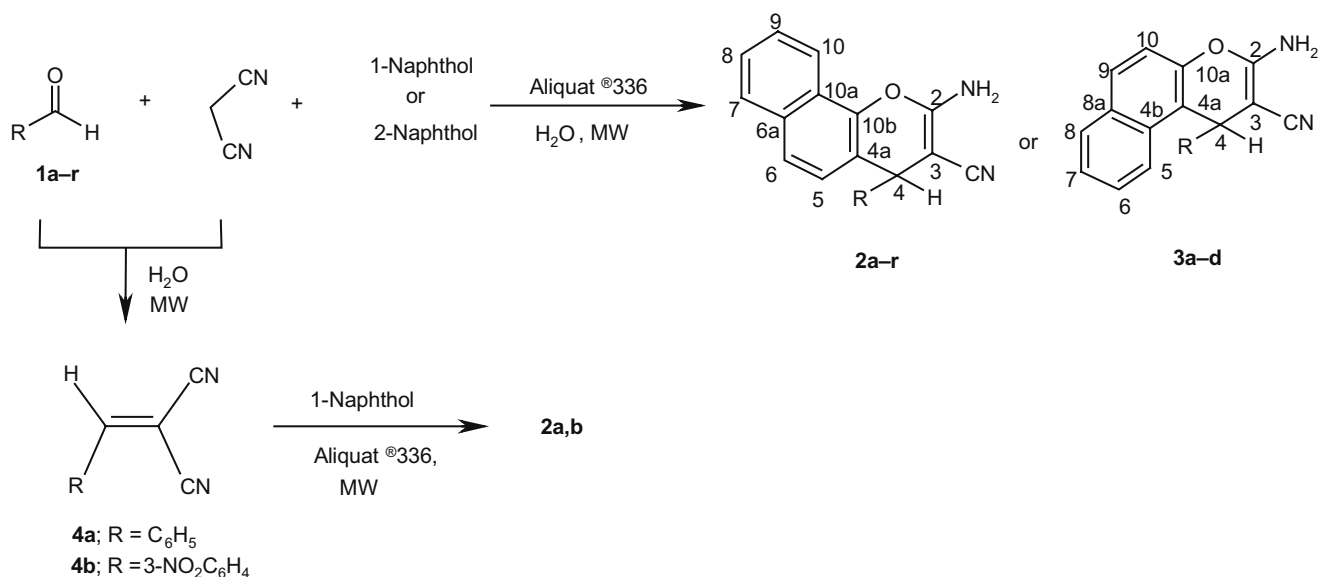
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Polyfunctionalised benzochromenes have useful biological and pharmacological activities¹⁻⁶ and this has stimulated our interest in their synthesis. Several syntheses have been reported previously involving the one-pot tandem condensation of an aldehyde, malononitrile and activated phenols using reagents such as ethanolic piperidine,⁷ Montmorillonite KSF clay,⁸ basic alumina,⁹ and KF-Al₂O₃ in refluxing ethanol.¹⁰ Recently green methodologies based on the use of triethylbenzylammonium chloride (TEBA),¹¹ tetrabutylammonium bromide (TBAB),¹² cetyltrimethylammonium chloride (CTACl)¹³ have been described. Although each method has its own merits there are various limitations such as long reaction times, complicated work-up procedures and effluent pollution. There is scope for better catalysts and an inexpensive, milder and quicker methodology, with the prospect for scale-up and a wider variation of substituents in the reactants.

Aliquat 336 is an effective phase transfer catalyst.¹⁴⁻¹⁶ In continuation of our work on its use in environmentally benign syntheses¹⁷ we now describe the results of our studies on the Aliquat 336 catalysed three-component condensation of aromatic aldehydes **1**, malononitrile and 1-naphthol or 2-naphthol to produce polyfunctionalised benzochromenes **2** and **3** under microwave irradiation in 80–95% overall yield (Scheme 1).

The reaction was carried out by simply mixing an aromatic aldehyde, malononitrile, a naphthol and the catalyst Aliquat 336 (0.5 mmol) in water (5 ml) under microwave irradiation for the time required for optimum yield (Table 1). This typical tandem reaction proceeds through the intermediacy of the α -cyanocinnamitrile **4** which is rapidly and quantitatively produced by the Knoevenagel condensation of malononitrile and an aromatic aldehyde with concomitant loss of water. It is reported that the Knoevenagel condensation can be carried out in water without adding any catalyst.¹⁸ Thus it is likely that the catalyst plays its role in the second step because the uncatalysed reaction affords only 30% yield for the same period of irradiation. The second step presumably involves *ortho*-C-alkylation by the electron deficient C=C moiety. Finally cyclisation via the nucleophilic addition of phenolic-OH group to the cyano moiety produces the 2-amino-2-chromenes.

To prove the intermediacy of α -cyanocinnamitrile enroute to 2-amino-2-chromenes we first prepared the α -cyanocinnamitriles of benzaldehyde and *m*-nitrobenzaldehyde separately with malononitrile in water alone under microwave heating. The isolated α -cyanocinnamitriles **4a** and **4b** were then separately treated with 1-naphthol in the presence of 0.5 mmol of Aliquat 336 in 5 ml water. The corresponding 2-amino-2-chromenes were formed in quantitative yield in 5 and 1 min respectively. The requirement



Scheme 1

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Table 1 Microwave-assisted synthesis of polyfunctionalised benzochromenes using Aliquat 336

Entry	R (Aldehyde)	Product	Time/min	Yields ^a /%	M.p./°C	
					Found	Reported ^{4, 22}
<i>From 1-Naphthol</i>						
1	C ₆ H ₅ (1a)	2a	8	85	205–207	206–207 ¹²
2	3–NO ₂ C ₆ H ₄ (1b)	2b	2.5	95	215	214–216 ¹²
3	2–NO ₂ C ₆ H ₄ (1c)	2c ^{8, 9}	5	87	208–210	^c
4	1–Furyl (1d)	2d	10	87	174–175	170–171 ²²
5	4–BrC ₆ H ₄ (1e)	2e ^b	5	90	234–236	—
6	3–BrC ₆ H ₄ (1f)	2f ^{2, 6}	12	91	224–226	^c
7	3–HOC ₆ H ₄ (1g)	2g ^b	8	82	234–237	—
8	4–HOC ₆ H ₄ (1h)	2h	12	83	250–252	249–251 ¹²
9	4–MeOC ₆ H ₄ (1i)	2i	16	85	183	182–183 ¹²
10	3,4(OMe) ₂ C ₆ H ₃ (1j)	2j	18	81	210–211	209–211 ^{19, 20}
11	2,3,4(OMe) ₃ C ₆ H ₂ (1k)	2k ^b	25	80	182–184	—
12	3,4,5(OMe) ₃ C ₆ H ₂ (1l)	2l	5	90	188–189	191–193 ⁴
13	4–OH–3–OMeC ₆ H ₃ (1m)	2m ^b	20	85	215–218	—
14	3–OBz–4–OMeC ₆ H ₃ (1n)	2n ^b	6	95	210–212	—
15	4–OBzC ₆ H ₄ (1o)	2o ^b	4	93	225–228	—
16	2–Br–4,5(OMe) ₂ C ₆ H ₂ (1p)	2p ^b	8	90	220–223	—
17	2–Br–4,5(O–CH ₂ –O)C ₆ H ₂ (1q)	2q ^b	5	92	245–248	—
18	4–ClC ₆ H ₄ (1r)	2r	3	93	231	231–232 ¹²
<i>From 2-Naphthol</i>						
19	C ₆ H ₅ (1a)	3a	8	85	280	278 ²¹
20	3–NO ₂ C ₆ H ₄ (1b)	3b	7	93	240–241	239–240 ^{19, 20}
21	2–NO ₂ C ₆ H ₄ (1c)	3c ^a	10	83	258–262	^c
22	1–Furyl (1d)	3d	20	82	219–222	225–226 ²²

^aIsolated yields. ^bNewly synthesised compounds. ^cM.p.s not available in the literature

for a shorter time is consistent with the intermediacy of an α -cyanocinnamitrile.

The scope of this methodology was then studied with a number of aromatic aldehydes. It was found that the method worked efficiently retaining the functional group such as nitro, hydroxyl, ether, chlorine and bromine in the aldehyde component intact. In each case, the yield of 2-amino-2-chromenes was high irrespective of the nature of the substituents. Thus the polar effects of substituents were not obvious under microwave heating. On the contrary, the indicated time in Table 1 for benzaldehyde, *m*-nitrobenzaldehyde, *o*-nitrobenzaldehyde and furfural reflects the greater reactivity of 1-naphthol compared to 2-naphthol in this reaction.

The methodology was then standardised for the amount of catalyst required to obtain a quantitative yield of the product. This was done first carrying out the reaction with benzaldehyde (5 mmol), malononitrile (5 mmol) and 1-naphthol (5 mmol) in the presence of 0.5 mmol Aliquat 336 in 5 ml water under microwave heating. In the following experiments the amount of the catalyst was increased to 1.0 mmol and 1.5 mmol keeping the amount of reactants same and subjected to microwave heating for the same period of time (Table 1). Table 2 shows that increasing amount of catalyst does not

Table 2 Standardisation of the amount of Aliquat 336 for the reaction of benzaldehyde with malononitrile and 1-naphthol

No. of observations	Amount of catalyst used/mmol	Isolated yield of product/%
1	0.5	85
2	1.0	86
3	1.5	86.5

Table 3 Recycling study

No. of cycles	Amount of catalyst used/mmol	Isolated yield of product/%
1	0.50	85
2	0.50	84
3	0.50	82

significantly alter yield of the product. Hence, the use of 0.5 mmol of the catalyst was satisfactory to obtain optimum yield of the product.

The reaction has been carried out with a reasonably large quantity of the reactants to examine its potential for scale-up. It has been observed that the reaction of benzaldehyde (20 mmol; 2.12 g), malononitrile (20 mmol; 1.32 g) and 1-naphthol (20 mmol; 2.88 g) in the presence of same quantity of Aliquat 336 (0.5 mmol) took 18 min to produce a maximum conversion into benzochromenes (82%) under microwave heating. Therefore, this process may have industrial application. By conventional heating method in the presence of 0.5 mmol Aliquat 336 in refluxing water, the same reaction took 5 h to produce quantitative yield of the product.

Recycling of Aliquat 336 was then tested by carrying out the reaction with benzaldehyde (5 mmol), malononitrile (5 mmol) and 1-naphthol (5 mmol) (Table 3). After each run, the reaction mixture was extracted with diethyl ether for 2–3 times to separate the products. The residual aqueous portion contained Aliquat 336, which was reused directly for the next run. It was found that Aliquat 336 can be recycled at least 3 times with little loss of activity (Table 3).

The structures of the newly synthesised compounds received support from extensive NMR studies.

Carbon–carbon connectivity mapping in **2g** and **2r** were further established by running the INADEQUATE experiment which was based on detection of natural ¹³C–¹³C coupled spin systems through the creation of double quantum coherence.^{23,24} Thus in a typical case of **2g** it was noted that C-4 methine carbon resonating at δ 41.1 was spin coupled to quaternary carbon resonances at δ 56.6 (C-3), 118.2 (C-4a) and 147.4 (C-1'). The unusually high field C-3 resonance at δ 56.6, in turn, was found to correlate with C-4 signal along with a quaternary carbon resonances at δ 160.4 (C-2) and 120.8 (CN). Again, C-4a signal showed correlations with the resonances for C-5 (δ 126.4) and C-10b (δ 142.9) along with that of C-4. Other important correlations that were noted were for signals for (i) C-5 with C-4a and C-6, (ii) C-6 with C-5 and C-6a, (iii) C-6a with C-7 and C-10a, (iv) C-7 with C-6a and C-8, (v) C-10 with C-9 and C-10a, (vi) C-1' with C-4,

C-2' and C-6', (vii) C-3' with C-2' and C-4', and (viii) C-5' with C-4' and C-6'. Signals for C-8 and C-9 were too close to be distinguished.

We have reported a reliable, rapid and environmentally benign method for the synthesis of various benzochromenes which involves the use of less toxic reagents in water as green solvent under microwave heating and is applicable to both 1- and 2-naphthols. The use of water not only simplifies the process but also makes the work-up procedure easier enough. In addition, high yields of the products, short reaction times, catalyst recycling combined with environment friendliness not only reflects its good industrial prospects but makes this method advantageous in comparison to other existing methods.

Experimental

Melting points (uncorrected) were recorded on a Toshniwal apparatus and were compared with those reported in the literature. IR spectra were recorded on a Perkin-Elmer FT IR-RXI Spectrophotometer using KBr pellets and ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker AV 300 NMR spectrometer in 5 mm BBO probe mostly in d_6 -DMSO and a few in CDCl_3 as solvent. Microanalytical data were recorded on a Perkin-Elmer 2400 II C, H, N, S analyser and mass spectra on a Qtof Micro YA 263 spectrometer.

General procedure

A mixture of aromatic aldehyde (5 mmol), malononitrile (5 mmol), naphthol (5 mmol) and Aliquat 336 (0.50 mmol) in water (5 ml) was placed inside a BPL-SANYO, 700T domestic microwave oven and irradiated for a specified time (Table 1) at 720 W. After completion of reaction (monitored by TLC), the reaction mixture was extracted with diethyl ether. The ether layer was then collected and subsequently dried over anhydrous Na_2SO_4 . Evaporation of the organic layer followed by purification by crystallisation from methanol afforded products (**2** and **3**).

2-Amino-3-cyano-4-(4-bromophenyl)-4H-benzo[h]chromene (2e): Yellowish white; amorphous powder; m.p. 234–236°C; ν_{max} (cm^{-1}): 3467, 3330, 3058, 2925, 2194, 1668, 1660, 1482, 1378, 1262, 1189; δ_{H} : 4.78 (s, 2H, NH_2), 4.85 (s, 1H, 4-H), 6.98 (d, $J = 8.6$ Hz, 1H, 5-ArH), 7.11 (complex d, $J = 8.5$ Hz, 2H, 2',6'-ArH), 7.44 (complex d, $J = 8.5$ Hz, 2H, 3',5'-ArH), 7.52 (d, $J = 8.6$ Hz, 1H, 6-ArH), 7.54 (m, 1H, 8-ArH), 7.58 (ddd, $J = 8.2$ Hz, 7.5 Hz, 1.5 Hz, 1H, 9-ArH), 7.80 (dd, $J = 7.5$ Hz, 1.7 Hz, 1H, 7-ArH), 8.18 (bd, $J = 8.2$ Hz, 1H, 10-ArH); δ_{C} : 41.0 (C-4), $^{13}\text{C}_{\text{CH}}$ = 140.2 Hz), 61.0 (C-3), 116.6 (C-4a), 119.4 (C-4'), 120.8 (C-10), $^{13}\text{C}_{\text{CH}}$ = 161.6 Hz), 121.4 (CN), 123.2 (C-10a), 124.8 (C-6), $^{13}\text{C}_{\text{CH}}$ = 162.2 Hz), 126.0 (C-5), $^{13}\text{C}_{\text{CH}}$ = 161.0 Hz), 126.8 (C-8), $^{13}\text{C}_{\text{CH}}$ = 160.6 Hz), 126.9 (C-9), $^{13}\text{C}_{\text{CH}}$ = 161.2 Hz), 127.8 (C-7), $^{13}\text{C}_{\text{CH}}$ = 160.4 Hz), 129.8 (C-2', C-6'), $^{13}\text{C}_{\text{CH}}$ = 165.6 Hz), 132.0 (C-3', C-5'), $^{13}\text{C}_{\text{CH}}$ = 165.4 Hz), 133.4 (C-6a), 143.3, 143.4 (C-1', C-10b), 159.0 (C-2); Anal. Found: C, 63.65; H, 3.5; N, 7.4. Calcd for $\text{C}_{20}\text{H}_{13}\text{ON}_2\text{Br}$: C, 63.7; H, 3.5; N, 7.4%.

2-Amino-3-cyano-4-(3-hydroxyphenyl)-4H-benzo[h]chromene (2g): Yellowish white, crystals; m.p. 234–237°C; ν_{max} (cm^{-1}): 3438, 3338, 2177, 1655, 1597, 1482, 1411, 1365, 1258, 1186; δ_{H} : 4.74 (s, 1H, 4-H), 6.58 (m, 2H, 2',4'-ArH), 6.67 (d, $J = 7.6$ Hz, 1H, 6'-ArH), 7.06 (m, 1H, 5'-ArH), 7.08 (d, $J = 7.3$ Hz, 1H, 5-ArH), 7.09 (s, 2H, NH_2), 7.52 (m, 1H, 8-ArH), 7.55 (d, $J = 7.9$ Hz, 1H, 6-ArH), 7.59 (m, 1H, 9-ArH), 7.84 (br.d, $J = 7.7$ Hz, 1H, 7-ArH), 8.21 (br.d, $J = 8.1$ Hz, 1H, 10-ArH), 9.37 (bs, 1H, OH); δ_{C} : 41.1 (C-4), 56.6 (C-3), 114.2 (C-4'), 114.6 (C-2'), 118.2 (C-4a), 118.6 (C-6'), 120.8 (CN), 120.9 (C-10), 122.9 (C-10a), 124.1 (C-6), 126.4 (C-5), 126.9 (C-8), 127.0 (C-9), 127.9 (C-7), 129.1 (C-5'), 132.9 (C-6a), 142.9 (C-10b), 147.4 (C-1'), 157.8 (C-3'), 160.4 (C-2); Anal. Found: C, 76.4; H, 4.5; N, 9.0. Calcd. for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_2$: C, 76.4; H, 4.5; N, 8.9%.

2-Amino-3-cyano-4-(2,3,4-trimethoxyphenyl)-4H-benzo[h]chromene (2k): Very light yellow; needles; m.p. 182–184°C; ν_{max} (cm^{-1}): 3430, 3328, 3204, 2932, 2192, 1664, 1601, 1494, 1460, 1406, 1385, 1272, 1193; δ_{H} : 3.58 (s, 3H, 2'-OCH₃), 3.68 (s, 3H, 3'-OCH₃), 3.69 (s, 3H, 4'-OCH₃), 4.96 (s, 1H, 4-H), 6.68 (d, $J = 8.6$ Hz, 1H, 5'-ArH), 6.78 (d, $J = 8.6$ Hz, 1H, 6'-ArH), 6.97 (d, $J = 8.4$ Hz, 1H, 5-ArH), 6.99 (bs, 2H, NH_2 , exchangeable with D_2O), 7.50 (m, 1H, 8-ArH), 7.51 (d, $J = 8.4$ Hz, 1H, 6-ArH), 7.57 (br.t, $J = 7.0$ Hz, 1H, 9-ArH), 7.81 (br.d, $J = 7.9$ Hz, 1H, 7-ArH), 8.20 (br. d, $J = 8.2$ Hz, 1H, 10-ArH); δ_{C} : 36.0 (C-4), $^{13}\text{C}_{\text{CH}}$ = 135.6 Hz), 56.0 (4'-OCH₃), $^{13}\text{C}_{\text{CH}}$ = 144.6 Hz), 56.1 (C-3), 60.5 (2'-OCH₃), $^{13}\text{C}_{\text{CH}}$ = 144.6 Hz), 61.0 (3'-OCH₃), $^{13}\text{C}_{\text{CH}}$ = 144.6 Hz), 108.3 (C-5'), $^{13}\text{C}_{\text{CH}}$ = 161.7 Hz), 118.2 (C-4a), 120.8 (C-10), $^{13}\text{C}_{\text{CH}}$ = 163.2 Hz), 120.9 (CN), 122.9

(C-10a), 123.9 (C-6), $^{13}\text{C}_{\text{CH}}$ = 164.9 Hz), 124.0 (C-6'), $^{13}\text{C}_{\text{CH}}$ = 164.9 Hz), 126.2 (C-5), $^{13}\text{C}_{\text{CH}}$ = 163.9 Hz), 126.8 (2C, C-8, C-9), $^{13}\text{C}_{\text{CH}}$ = 161.0 Hz), 127.8 (C-7), $^{13}\text{C}_{\text{CH}}$ = 160.2 Hz), 131.1 (C-1'), 132.8 (C-6a), 141.9 (C-3'), 143.1 (C-10b), 151.3 (C-2'), 152.7 (C-4'), 160.5 (C-2); Anal. Found: C, 71.1; H, 5.2; N, 7.3. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_4\text{N}_2$: C, 71.1; H, 5.2; N, 7.2%.

2-Amino-3-cyano-4-(4-hydroxy-3-methoxyphenyl)-4H-benzo[h]chromene (2m): Yellow; amorphous powder; m.p. 215–218°C; ν_{max} (cm^{-1}): 3460, 3338, 2191, 1665, 1604, 1511, 1442, 1377, 1269, 1106; δ_{H} : 3.65 (s, 3H, OCH₃), 4.71 (s, 1H, 4-H), 6.53 (dd, $J = 8.1$ Hz, $J = 1.8$ Hz, 1H, 6'-ArH), 6.65 (d, $J = 8.2$ Hz, 1H, 5'-ArH), 6.78 (bs, 1H, 2'-ArH), 6.96 (s, 2H, NH_2), 7.08 (d, $J = 8.5$ Hz, 1H, 5-ArH), 7.49 (m, 1H, 8-ArH), 7.53 (d, $J = 8.5$ Hz, 1H, 6-ArH), 7.55 (m, 1H, 9-ArH), 7.81 (d, $J = 7.9$ Hz, 1H, 7-ArH), 8.17 (d, $J = 7.9$ Hz, 1H, 10-ArH), 9.02 (bs, 1H, OH); δ_{C} : 41.0 (C-4), 56.2 (OCH₃), 57.3 (C-3), 112.4 (C-2'), 116.2 (C-5'), 118.8 (C-4a), 120.6 (C-6'), 121.3 (C-10), 123.3 (C-10a), 124.5 (C-6), 126.8 (C-5), 127.4 (2C, C-8, C-9), 128.2 (C-7), 133.2 (C-6a), 137.4 (C-1'), 143.0 (C-10b), 145.9 (C-4'), 148.1 (C-3'), 160.7 (C-2); Anal. Found: C, 73.2; H, 4.7; N, 8.1. Calcd. for $\text{C}_{21}\text{H}_{16}\text{O}_3\text{N}_2$: C, 73.2; H, 4.7; N, 8.1%.

2-Amino-3-cyano-4-(3-benzyloxy-4-methoxyphenyl)-4H-benzo[h]chromene (2n): Yellowish white; amorphous; m.p. 210–212°C; ν_{max} (cm^{-1}): 3448, 3326, 2935, 2196, 1665, 1602, 1510, 1378, 1263, 1141; δ_{H} : 3.64 (s, 3H, OCH₃), 4.71 (s, 1H, 4-H), 4.89, 4.95 (pair of d, $J = 12$ Hz, 1H each, OCH₂), 6.71 (bd, $J = 8.3$ Hz, 1H, 6'-ArH), 6.83 (bs, 1H, 2'-ArH), 6.86 (d, $J = 8.0$ Hz, 1H, 5'-ArH), 6.98 (d, $J = 8.6$ Hz, 1H, 5-ArH), 7.00 (bs, 2H, NH_2), 7.15–7.30 (m, 5H, 2", 3", 4", 5", 6'-ArH), 7.48 (d, $J = 8.6$ Hz, 1H, 6-ArH), 7.51 (m, 1H, 8-ArH), 7.57 (m, 1H, 9-ArH), 7.82 (d, $J = 7.8$ Hz, 1H, 7-ArH), 8.18 (d, $J = 8.1$ Hz, 1H, 10-ArH); δ_{C} : 40.9 (C-4), 56.2 (OCH₃), 57.0 (C-3), 70.6 (C-7"), 112.9 (C-5'), 114.2 (C-2'), 118.6 (C-4a), 120.7 (C-6'), 121.3 (2C, C-10, CN), 123.3 (C-10a), 124.5 (C-6), 126.7 (C-5), 127.3 (C-8), 127.4 (C-9), 128.2 (C-7), 128.5 (C-4'), 128.6 (2C, C-2', C-6'), 128.9 (2C, C-3', C-5'), 133.2 (C-6a), 137.3 (C-1'), 138.6 (C-1'), 143.0 (C-10b), 148.1 (C-3'), 148.8 (C-4'), 160.8 (C-2); Anal. Found: C, 77.4; H, 5.1; N, 6.4. Calcd. for $\text{C}_{28}\text{H}_{22}\text{O}_3\text{N}_2$: C, 77.4; H, 5.1; N, 6.45%.

2-Amino-3-cyano-4-(4-benzyloxyphenyl)-4H-benzo[h]chromene (2o): White solid; amorphous; m.p. 225–228°C; ν_{max} (cm^{-1}): 3462, 3329, 2194, 1665, 1603, 1508, 1377, 1236, 1180; δ_{H} : 4.74 (s, 1H, 4-H), 4.96 (s, 2H, OCH₂), 6.88 (d, $J = 8.6$ Hz, 2H, 3',5'-ArH), 6.99 (bs, 2H, NH_2), 7.01 (d, $J = 8.5$ Hz, 1H, 5-ArH), 7.08 (d, $J = 8.6$ Hz, 2H, 2',6'-ArH), 7.20–7.40 (m, 5H, 2", 3", 4", 5", 6'-ArH), 7.28 (d, $J = 7.7$ Hz, 2H, 2", 6'-ArH), 7.49 (m, 1H, 8-ArH), 7.53 (d, $J = 8.5$ Hz, 1H, 6-ArH), 7.55 (m, 1H, 9-ArH), 7.80 (d, $J = 7.7$ Hz, 1H, 7-ArH), 8.17 (d, $J = 8.0$ Hz, 1H, 10-ArH); δ_{C} : 40.6 (C-4), 57.2 (C-3), 69.8 (C-7), 115.5 (2C, C-3', C-5'), 118.7 (C-4a), 121.3 (2C, C-10, CN), 123.3 (C-10a), 124.6 (C-6), 126.8 (C-5), 127.4 (C-8), 127.5 (C-9), 128.3 (3C, C-3', C-4', 5'), 128.5 (C-7), 129.1 (2C, C-2', C-6'), 129.3 (C-2', C-6'), 133.2 (C-6a), 137.5 (C-1'), 138.6 (C-1'), 143.1 (C-10b), 157.9 (C-4'), 160.7 (C-2); m/z , M^+Na (%), Found: 427.1426 (100). Calcd. for $\text{C}_{27}\text{H}_{20}\text{O}_2\text{N}_2\text{Na}$: 427.1422.

2-Amino-3-cyano-4-(2-bromo-4,5-dimethoxyphenyl)-4H-benzo[h]chromene (2p): Greenish yellow; crystals; m.p. 220–223°C; ν_{max} (cm^{-1}): 3449, 3350, 2938, 2183, 1629, 1500, 1376, 1242, 1190; δ_{H} : 3.47 (s, 3H, 4'-OCH₃), 3.63 (s, 3H, 5'-OCH₃), 5.21 (s, 1H, 4-H), 6.69 (s, 1H, 6'-ArH), 6.91 (d, $J = 8.5$ Hz, 1H, 5-ArH), 7.04 (bs, 3H, 3'-ArH, NH_2), 7.49 (m, 1H, 8-ArH), 7.51 (d, $J = 8.4$ Hz, 1H, 6-ArH), 7.55 (m, 1H, 9-ArH), 7.79 (d, $J = 7.8$ Hz, 1H, 7-ArH), 8.18 (d, $J = 8.1$ Hz, 1H, 10-ArH); δ_{C} : 40.9 (C-4), 55.8 (C-3), 56.3 (OCH₃), 56.5 (OCH₃), 113.4 (C-2'), 114.3 (C-6'), 116.3 (C-3'), 117.0 (C-4a), 120.9 (CN), 121.4 (C-10), 123.2 (C-10a), 124.6 (C-6), 125.9 (C-5), 127.4 (C-8), 127.6 (C-9), 128.3 (C-7), 133.4 (C-6a), 135.8 (C-1'), 143.4 (C-10b), 149.2 (C-4'), 149.3 (C-5'), 160.9 (C-2); m/z , M^+Na (%), Found: 461.0226 (100), 459.0300 (98). Calcd. for $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}_2\text{BrNa}$: 461.0303, 459.0320.

2-Amino-3-cyano-4-(2-bromo-4,5-dioxymethylenephenyl)-4H-benzo[h]chromene (2q): White solid; amorphous; m.p. 245–248°C; ν_{max} (KBr pellets, cm^{-1}): 3417, 3327, 2196, 1661, 1611, 1478, 1379, 1231, 1105; δ_{H} : 5.29 (s, 1H, 4-H), 5.94 and 5.99 (2 x s, 1H each, O-CH₂-O), 6.63 (s, 1H, 6-ArH), 6.95 (d, $J = 8.6$ Hz, 1H, 5-ArH), 7.12 (bs, 2H, NH_2), 7.15 (s, 1H, 3'-ArH), 7.53 (m, 1H, 8-ArH), 7.56 (d, $J = 8.6$ Hz, 1H, 6-ArH), 7.59 (m, 1H, 9-ArH), 7.84 (d, $J = 8.1$ Hz, 1H, 7-ArH), 8.19 (d, $J = 8.1$ Hz, 1H, 10-ArH); δ_{C} : 40.5 (C-4), 55.4 (C-3), 102.4 (O-CH₂-O), 110.1 (C-6'), 112.3 (C-3'), 112.9 (C-2'), 116.8 (C-4a), 120.2 (CN), 121.0 (C-10), 122.9 (C-10a), 124.3 (C-6), 125.4 (C-5), 127.0 (C-8), 127.2 (C-9), 127.9 (C-7), 133.1 (C-6a), 137.4 (C-1'), 143.0 (C-10b), 147.6 (C-4'), 148.1 (C-5'), 160.4 (C-2); m/z , M^+Na (%), Found: 444.9915 (35), 443.0001 (38). Calcd. for $\text{C}_{21}\text{H}_{13}\text{O}_3\text{N}_2\text{BrNa}$: 444.9990, 443.0007.

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