A green method for the synthesis of novel benzo[*b*]pyran derivatives in an ionic liquid

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A series of novel 2-amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4-aryl-4*H*-benzo[*b*]pyran-3-carbonitriles was obtained from the reaction of 2-(1-arylethylidene)malononitrile and 5,5-dimethylcyclohexane-1,3-dione in an ionic liquid at 90°C. This method had the advantages of operational simplicity, mild reaction conditions and an environmentally benign procedure.

Keywords: benzopyran, ionic liquid, 5,5-dimethylcyclohexane-1,3-dione

In recent times, room temperature ionic liquids (RTILs), especially those based on the 1,3-dialkylimidazolium salts, have shown great promise as attractive alternatives to conventional solvents. They possess the unique advantages of high thermal stability, negligible vapour pressure, immiscibility with a number of organic solvents and recyclability. In many cases, the products are weakly soluble in the ionic phase so that the products can be easily separated by simple extraction. Ionic liquids have been used as solvents for a large number of organic transformations.[1-5]

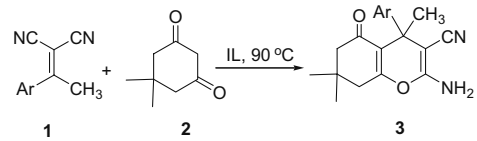
Benzopyran and its derivatives are very useful compounds in various fields of chemistry and in medicine. This heterocyclic moiety has found broad application in drug development for the treatment of bone defects and injuries,[6] smooth muscle cell-rich vascular lesions,[7] cancer in animals[8] and infectious diseases.[9] 2-Aminobenzo[b]pyran is one of a number of important benzopyrans, which have received considerable attention due to their wide range of useful biological properties, which include antimicrobial activity,[10,11] antibacterial activity,[12] antiapoptotic[13] activity and molluscicidal activity.[14] Accordingly, novel strategies for the synthesis of 2-aminobenzopyran derivatives continue to receive much attention in the field of synthetic organic chemistry.[15-21] They have mainly been synthesised from the reactions of active compounds such as those containing 1,3-dicarboxyl groups and naphthalenol, with an α,β-unsaturated dinitrile or cyanoacetate, or by three component reactions of benzaldehyde, malonodinitrile (or cyanoacetate) and active compounds.

However, it should be noted that the known 2-aminobenzopyrans from the above-mentioned reactions only contained one non-hydrogen group such as a phenyl group on the 4-position, the other group was always a hydrogen atom. In order to solve the problem of obtaining two non-hydrogen groups on the 4-position, we report here the synthesis of 2-amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4-aryl-4*H*-benzo[b] pyran-3-carbonitrile in an ionic liquid.

Results and discussion

2-(1-Arylethylidene)malononitrile **1** and 5,5-dimethyl cyclohexane-1,3-dione **2** were treated in an ionic liquid at 90°C and 2-amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4-aryl-4*H*-benzo[b]pyran-3-carbonitrile derivatives **3** were obtained in good yields (Scheme 1).

Firstly, we tried to perform the three component reaction between acetophenone, malonodinitrile and 5,5-dimethylcyclohexane-1,3-dione, but failed. Subsequently, we synthesised the 2-(1-arylethylidene)malononitriles **1** from acetophenones and malonodinitrile and then reacted them with **2**. The desireds product were obtained in good yields. The optimisation of the reaction conditions, including reaction temperature and solvent, was investigated using 2-(1-(4-nitrophenyl)ethylidene)malononitrile and **2** as model reactants. As summarised in Table 1, the results showed that at room temperature only trace amounts of product were found by TLC (Table 1, entry 1). To our delight, the reaction proceeded smoothly in good yield at 90°C. Moreover, different ionic liquids were tested as reaction media and it was observed that [bmim$^+$] [BF_4^-] was the preferred ionic liquid for the reaction (Table 1, entries 3–8). In addition, EtOH and DMF were also tested as solvents for this reaction. It was found that only a trace amount of product was obtained when EtOH alone was used and that only 52% was isolated in DMF (Table 1, entries 9–10). A little piperidine was added to the EtOH or [bmim$^+$][BF_4^-] solvents to significantly increase or slightly decrease the yields respectively (Table 1, entries 11–12).



Scheme 1

After the reaction was completed, the reaction mixtures were cooled to room temperature. Water (5 mL) was then added to the mixture and the solid was isolated by filtration. The water in the filtrate was removed by evaporation at reduced pressure at 80°C for 4 h and the ionic liquid in the filtrate could be recycled. The recovered ionic liquid could be directly used for reactions involving the same substrate. Alternatively, if the

Table 1 Synthesis of **3a** under different reaction conditions[a]

Entry	Temp./°C	Ionic liquid[b]	Yield[c]/%
1	R.t.	[bmim$^+$][BF_4^-]	Trace
2	50	[bmim$^+$][BF_4^-]	58
3	**90**	**[bmim$^+$][BF_4^-]**	**85**
4	90	[emim$^+$] Br^-	77
5	90	[pmim$^+$] Br^-	79
6	90	[bmim$^+$]Br^-	78
7	90	[emim$^+$][BF_4^-]	82
8	90	[pmim$^+$][BF_4^-]	80
9	Reflux	EtOH	Trace
10	90	DMF	52
11	Reflux	Piperidine/EtOH	72
12	90	Piperidine/[bmim$^+$][BF_4^-]	78

[a]Reaction conditions: ionic liquid (2 mL), 2-(1-(4-nitrophenyl) ethylidene)malononitrile (0.426 g, 2 mmol) and **2** (0.280 g, 2 mmol).
[b]bmim = 1-butyl-3-methylimidazolium; emim = 1-ethyl-3-methylimidazolium; pmim = 1-methyl-3- propylimidazolium.
[c]Isolated yields.

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Table 2 The reactions of 2-(1-arylethylidene) malononitrile and 5,5-dimethyl cyclohexane-1,3-dione in an ionic liquid[a]

Entry	Ar	Products	Time/h	Yields/%[b]
1	4-$NO_2C_6H_4$	**3a**	12	85
2	3-$OMeC_6H_4$	**3b**	14	82
3	4-FC_6H_4	**3c**	12	88
4	4-ClC_6H_4	**3d**	15	81
5	2-naphthoyl	**3e**	14	85
6	4-benzyloxyphenyl	**3f**	16	78
7	4-$OMeC_6H_4$	**3g**	16	79
8	4-MeC_6H_4	**3h**	15	83
9	3-BrC_6H_4	**3i**	15	81
10	4-BrC_6H_4	**3j**	15	80
11	C_6H_5	**3k**	14	87

[a]Reaction conditions: ionic liquid (2 mL), **1** (2 mmol) and **2** (0.280 g, 2 mmol).
[b]Isolated yields.

ionic liquid was used for reactions with different substrates, it was washed with ethyl acetate, followed by evaporation at 80 °C under reduced pressure for 3 h. Investigations using 2-(1-(4-nitrophenyl)ethylidene)malononitrile and **2** as model substrates proved the successful reuse of the ionic liquid. Even in the fourth cycle the yield (83%) of product **3a** was fairly good.

According to the optimised conditions, we next examined the utility of this process (Scheme 3) to synthesise a range of benzo[*b*]pyrans **3**. Various 2-(1-arylethylidene) malononitriles **1**, bearing either electron-withdrawing groups (such as halide or nitro) or electron-donating groups (such as alkyl or alkoxyl), were subjected to reaction with **2** to give the corresponding benzo[b]pyran derivatives **3** in good yields (Table 2).

Conclusion

In conclusion, we have reported a green method of synthesising novel 2-aminobenzo[b]pyran derivatives bearing two non-hydrogen groups on the 4-position from the reaction of 2-(1-arylethylidene)malononitrile and 5,5-dimethylcyclohexane-1,3-dione in an ionic liquid at 90 °C. The noteworthy features of this procedure are mild reaction conditions, reaction in one-pot, good yields, operational simplicity and an environmentally friendly procedure. Also, [bmim$^+$] [BF_4^-] could be reused several times without significant loss of activity.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr pellets. ^{1}H NMR spectra were obtained from solution in DMSO-d_6 with Me_4Si as an internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker-micro-TOF-Q-MS analyser.

General procedure for the syntheses of 2-amino-5,6,7,8-tetrahydro-4,7,7- trimethyl-5-oxo-4-aryl-4H-benzo[b]pyran-3-carbonitrile **3**
A dry 50 mL flask was charged with 2-(1-arylethylidene)malononitrile (2.0 mmol), 5,5-dimethylcyclohexane-1,3-dione (0.280 g, 2.0 mmol), and [bmim$^+$][BF_4^-] (2 mL). The reaction mixture was stirred at 90 °C for 12–16 h, and then cooled to room temperature. The generated yellow solid was filtered off, and the ionic liquid in the filtrate was then recovered for reuse by heating at 80 °C for several hours under reduced pressure. The crude yellow products were washed with water and purified by recrystallisation from DMF and water, followed by being dried at 80 °C for several hours under reduced pressure to give **3**.

2-Amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3a**): M.p. 201–202 °C (Lit.[21] 195–196 °C). ^{1}H NMR (DMSO-d_6, δ, ppm): 1.05 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 2.10 (d, J = 15.6 Hz, 1H, CH), 2.18 (d, J = 15.6 Hz, 1H, CH), 2.50–2.55 (m, 2H, CH_2), 7.02 (s, 2H, NH_2), 7.55 (d, J = 8.8 Hz, 2H, ArH), 8.15 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.5, 27.4, 27.5, 30.7, 31.5, 38.2, 51.0, 64.4, 115.4, 118.5, 122.9, 127.8, 145.4, 155.7, 156.8, 162.0, 195.8. IR (KBr, ν, cm^{-1}): 3397, 3329, 2963, 2194, 1659, 1603, 1519, 1459, 1411, 1349, 1317, 1212, 1167, 1112, 1049, 1012, 862; HRMS [Found: *m/z* 376.1254, Calcd for $C_{19}H_{19}N_3NaO_4$: (M + Na$^+$) 376.1273].

2-Amino-5,6,7,8-tetrahydro-4-(3-methoxyphenyl)-4,7,7-trimethyl-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3b**): M.p. 219–221 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): 1.01 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.09 (d, J = 15.6 Hz, 1H, CH), 2.18 (d, J = 15.6 Hz, 1H, CH), 2.50–2.55 (m, 2H, CH_2), 3.72 (s, 3H, CH_3O), 6.72–6.74 (m, 2H, ArH), 6.78 (s, 2H, NH_2), 6.82 (d, J = 8.0 Hz, 1H, ArH), 7.17–7.22 (m, 1H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.4, 27.3, 27.6, 31.4, 37.6, 40.1, 51.3, 54.8, 65.9, 110.2, 112.9, 115.9, 118.8, 128.7, 149.6, 156.4, 158.8, 161.3, 195.7. IR (KBr, ν, cm^{-1}): 3409, 3329, 3007, 2954, 2833, 2193, 1656, 1601, 1493, 1467, 1428, 1406, 1389, 1352, 1318, 1288, 1254, 1208, 1168, 1044, 986, 965, 857, 776, 764,704; HRMS [Found: *m/z* 361.1514, Calcd for $C_{20}H_{22}N_2NaO_3$: (M + Na$^+$) 361.1528].

2-Amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3c**): M.p. 219–221 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): '0.98 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.07 (d, J = 15.6 Hz, 1H, CH), 2.16 (d, J = 15.6 Hz, 1H, CH), 2.46–2.56 (m, 2H, CH_2), 6.86 (s, 2H, NH_2), 7.06–7.10 (m, 2H, ArH), 7.26–7.29 (m, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.7, 27.4, 30.8, 31.4, 37.4, 40.1, 51.3, 65.7, 114.1, 114.3, 115.8, 128.2, 128.3, 144.1 156.4, 159.0, 161.3 162.4. IR (KBr, ν, cm^{-1}): 3400, 3327, 3009, 2960, 2874, 2195, 1664, 1640, 1508, 1471, 1408, 1350, 1316, 1212, 1164, 1087, 1047, 984, 962, 917, 892, 845; HRMS [Found: *m/z* 349.1320, Calcd for $C_{19}H_{19}FN_2NaO_2$: (M + Na$^+$) 349.1328].

2-Amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3d**): M.p. 205–206 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): 0.99 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.08 (d, J = 15.6 Hz, 1H, CH), 2.17 (d, J = 15.6 Hz, 1H, CH), 2.50–2.55 (m, 2H, CH_2), 6.86 (s, 2H, NH_2), 7.27 (d, J = 8.8 Hz, 2H, ArH), 7.32 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.5, 27.4, 30.7, 31.4, 37.6, 40.1, 51.2, 65.4, 115.7, 118.7, 127.6, 128.3, 130.3, 147.0, 156.5, 161.5, 195.7. IR (KBr, ν, cm^{-1}): 3392, 3323, 3013, 2946, 2888, 2195, 1715, 1694, 1682, 1660, 1651, 1645, 1634, 1605, 1493, 1463, 1409, 1351, 1317, 1277, 1211, 1169, 1093, 1047, 1011, 985, 963, 844; HRMS [Found: *m/z* 365.1012, Calcd for $C_{19}H_{19}{}^{35}ClN_2NaO_2$: (M + Na$^+$) 365.1033]. The expected MS intensity pattern due to Cl isotopes was observed.

2-Amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-4-(naphthalen-2-yl)-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3e**)*:* M.p. 269–270 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): 1.01 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 2.06 (d, J = 15.6 Hz, 1H, CH), 2.17 (d, J = 15.6 Hz, 1H, CH), 2.50–2.55 (m, 2H, CH_2), 6.87 (s, 2H, NH_2), 7.37–7. 39 (m, 1H, ArH), 7.47–7.50 (m, 2H, ArH), 7.79–7.85 (m, 3H, ArH), 7.91–7.96 (m, 1H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.5, 27.3, 27.7, 31.5, 38.0, 40.2, 51.3, 65.6, 115.8, 118.8, 123.9, 125.6, 125.7, 126.0, 127.2, 127.3, 128.0, 131.3, 132.5, 145.1, 156.5, 161.5, 195.8. IR (KBr, ν, cm^{-1}): 3390, 3325, 3053, 3026, 2957, 2873, 2193, 1656, 1606, 1509, 1458, 1410, 1391, 1373, 1352, 1316, 1210, 1168, 1129, 1048, 986, 888, 855, 820, 791, 739, 693; HRMS [Found: *m/z* 381.1558, Calcd for $C_{23}H_{22}N_2NaO_2$: (M + Na$^+$), 381.1579].

2-Amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-4-(4-benzyloxyphenyl)-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3f**): M.p. 230–232 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): 0.98 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.07 (d, J = 15.6 Hz, 1H, CH), 2.16 (d, J = 15.6 Hz, 1H, CH), 2.50–2.55 (m, 2H, CH_2), 5.05 (s, 2H, CH_2), 6.74 (s, 2H, NH_2), 6.91 (d, J = 8.8 Hz, 2H, ArH), 7.16 (d, J = 8.8 Hz, 2H, ArH), 7.38–7.42 (m, 3H, ArH), 7.46 (d, J = 7.2 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.6, 27.4, 27.5, 31.4, 37.2, 40.2, 51.4, 66.2, 69.2, 113.7, 116.0, 118.9, 127.5, 127.7, 127.8, 128.4, 137.2, 140.3, 156.26, 156.29, 161.0, 195.7. IR (KBr, ν, cm^{-1}): 3304, 3327, 2953, 2902, 2862, 2193, 1666, 1604, 1508, 1468, 1456, 1408, 1370, 1350, 1316, 1238, 1238, 1177, 1066, 1046, 1014, 983, 962, 918, 865, 837; HRMS [Found: *m/z* 437.1841, Calcd for $C_{26}H_{26}N_2NaO_3$: (M + Na$^+$) 437.1841].

2-Amino-5,6,7,8-tetrahydro-4-(4-methoxyphenyl)-4,7,7-trimethyl-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3g**): M.p. 243–245 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): 0.99 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 2.06 (d, J = 15.6 Hz, 1H, CH), 2.16 (d, J = 15.6 Hz, 1H, CH), 2.50–2.55 (m, 2H, CH_2), 3.73 (s, 3H, CH_3O), 6.69 (s, 2H, NH_2), 6.82 (d, J = 8.4 Hz, 2H, ArH), 7.16 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.6, 27.3, 27.6, 31.4, 37.1, 40.2, 51.4, 54.9, 66.2, 112.9, 116.0, 118.9, 127.4, 140.1, 156.3, 157.0, 160.9, 195.7. IR (KBr, ν, cm^{-1}): 3396, 3327, 2969, 2931, 2903, 2843, 2192, 1661, 1605, 1511, 1463, 1440, 1408, 1390, 1371, 1351, 1319, 1295, 1256, 1208, 1179, 1067, 1046, 1030, 981, 837; HRMS [Found: *m/z* 361.1526, Calcd for $C_{20}H_{22}N_2NaO_3$: (M + Na$^+$) 361.1528].

2-Amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4-p-tolyl-4H-benzo[b]pyran-3-carbonitrile (**3h**): M.p. 213–215 °C; ^{1}H NMR (DMSO-d_6, δ, ppm): 0.99 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 2.06 (d, J = 15.6 Hz, 1H, CH), 2.16 (d, J = 15.6 Hz, 1H, CH), 2.25 (s, 3H, CH_3), 2.51–2.58 (m, 2H, CH_2), 6.74 (s, 2H, NH_2), 7.06 (d, J = 8.4 Hz, 2H, ArH), 7.13 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 20.5, 27.3, 27.6, 31.4, 37.4, 40.1, 51.4, 66.1, 116.0, 118.8, 126.2, 128.3, 134.5, 145.0, 156.3, 161.0, 195.7. IR (KBr, ν, cm^{-1}): 3396, 3326, 3017, 2962, 2195, 1715, 1655, 1605, 1511, 1460, 1408, 1391, 1351, 1282, 1211, 1169, 1064, 1047, 1018, 986, 963, 918, 835; HRMS [Found: *m/z* 345.1579, Calcd for $C_{20}H_{22}N_2NaO_2$: (M + Na$^+$) 345.1579].

2-Amino-4-(3-bromophenyl)-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3i**): M.p. 222–224 °C; ^{1}H NMR (DMSO-d$_6$, δ, ppm): 1.00 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.10 (d, J = 15.6 Hz, 1H, CH), 2.19 (d, J = 15.6 Hz, 1H, CH), 2.48–2.59 (m, 2H, CH_2), 6.90 (s, 2H, NH_2), 7.26 (d, J = 6.8 Hz, 2H, ArH), 7.35–7.37 (m, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.4, 27.3, 27.5, 31.5, 37.8, 40.1, 51.2, 65.2, 115.5, 118.6, 121.2, 125.6, 128.6, 129.0, 129.9, 150.7, 156.6, 161.7, 195.7. IR (KBr, ν, cm^{-1}): 3393, 3327, 2967, 2890, 2194, 1656, 1605, 1569, 1468, 1416, 1389, 1371, 1350, 1317, 1272, 1211, 1166, 1123, 1048, 986, 966, 961, 880, 804, 764, 713, 698; HRMS [Found: *m/z* 409.0518, Calcd for $C_{19}H_{19}{}^{79}BrN_2NaO_2$: (M + Na$^+$) 409.0528]. The expected MS intensity pattern due to Br isotopes was observed.

2-Amino-4-(4-bromophenyl)-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4H-benzo[b]pyran-3-carbonitrile (**3j**): M.p. 213–214 °C; ^{1}H NMR (DMSO-d$_6$, δ, ppm): 0.99 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.08 (d, J = 15.6 Hz, 1H, CH), 2.17 (d, J = 15.6 Hz, 1H, CH), 2.51–2.56 (m, 2H, CH_2), 6.88 (s, 2H, NH_2), 7.21 (d, J = 8.4 Hz, 2H, ArH), 7.46 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.4, 27.4, 27.5, 31.4, 37.6, 40.1, 51.2, 65.3, 115.6, 118.7, 118.8, 128.7, 130.5, 147.4, 156.5, 162.4, 195.7. IR (KBr, ν, cm^{-1}): 3393, 3325, 3013, 2963, 2872, 2194, 1715, 1656, 1604, 1488, 1464, 1410, 1396, 1351, 1317, 1276, 1211, 1169, 1078, 1048, 1008, 986, 963, 841; HRMS [Found: *m/z* 409.0519, Calcd for $C_{19}H_{19}{}^{79}BrN_2NaO_2$: (M + Na$^+$) 409.0528]. The expected MS intensity pattern due to Br isotopes was observed.

2-Amino-5,6,7,8-tetrahydro-4,7,7-trimethyl-5-oxo-4-phenyl-4H-benzo[b]pyran-3-carbonitrile (**3k**): M.p. 213–214 °C; ^{1}H NMR (DMSO-d$_6$, δ, ppm): 1.00 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 2.08 (d, J = 15.6 Hz, 1H, CH), 2.17 (d, J = 15.6 Hz, 1H, CH), 2.51–2.58 (m, 2H, CH_2), 6.78 (s, 2H, NH_2), 7.12–7.16 (m, 1H, ArH), 7.24–7.29 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, δ, ppm): 25.4, 27.4, 27.5, 31.4, 37.7, 40.1, 51.3, 66.0, 116.0, 118.8, 125.6, 126.3, 127.7, 147.9, 156.4, 161.3, 195.7. IR (KBr, ν, cm^{-1}): 3398, 3326, 3060, 3008, 2962, 2871, 2196, 1681, 1605, 1491, 1447, 1407, 1350, 1316, 1267, 1211, 1167, 1047, 984, 961, 917, 808, 741, 699; [Found: *m/z* 331.1417, Calcd for $C_{19}H_{20}NaN_2O_2$: (M + Na$^+$) 331.1422].

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