An Efficient Synthesis of Indeno[1,2-*b*]pyridine and Benzo[*h*]quinoline Derivatives Under Solvent-Free Conditions

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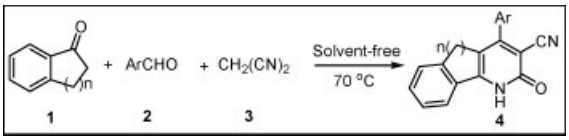

An efficient and convenient multicomponent reaction for the preparation of 4-aryl-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile and 4-aryl-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile derivatives by the 2,3-dihydroinden-1-one or 3,4-dihydronaphthalen-1(2*H*)-one, aromatic aldehydes, and malononitrile in the presence of sodium hydroxide under solvent-free condition is reported. The short reaction time coupled with the simplicity of the reaction procedure makes this method one of the most efficient methods for the synthesis of these classes of compounds.

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INTRODUCTION

At the new century begins, organic synthetic chemists are placing a greater importance on protecting the environment. A shift in emphasis in chemistry is apparent with the desire to develop more environmentally friendly routes to a myriad of materials. This shift is most apparent in the growth of green chemistry [1–3]. Green chemistry approaches not only hold out significant potential for reduction of by-products, a reduction in the waste produced and lowering of energy costs, but also in the development of new methodologies toward previously unobtainable materials, using existing technologies [4]. Solvent-free organic synthesis [5], as one of efficient synthesis strategies of green chemistry, has caused great interest by chemists in recent years. For they have the many advantages, such as high efficiency and selectivity, easy separation and purification, and mild reaction conditions. Furthermore, the organic solvent could be avoided in this process, and it was very important of protecting the environment.

Substituted six-membered lactams have attracted the attention of synthetic organic chemists for many years because these structural features are found in a wide variety of naturally occurring alkaloids [6]. For the compounds with these scaffolds have been shown significant pharmacological properties, medicinal chemists often incorporate these motifs in the design of novel biologically active drugs. For example, arnrinone and milrinone are these type drugs [7] and that have been found to display effective activities on therapy of myocardial infarction. Because of importance of these kinds of compounds, development of a general and efficient synthetic strategy to synthesize those compounds is still desired. Although several synthetic methodologies directed toward the preparation of six-membered lactams have been reported [8], they had many disadvantages, such as long reaction times, low yields, and forces reaction conditions. Especially, in reported reactions, the organic solvents were necessary. In continuation of our research to prepare organic compounds under solvent-free conditions [9], herein, we reported a simple and efficient process to synthesize six-membered lactams, indeno[1,2-*b*]pyridine and benzo[*h*]quinoline derivatives under solvent-free conditions.

RESULTS AND DISCUSSION

The operation of preparation these derivatives could be carried out as follows: 2,3-dihydroinden-1-one, aromatic aldehydes, and malononitrile were put into a round flask, in the presence of a small amount NaOH under solvent-free conditions at 70°C, and corresponding products, 4-aryl-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-arbo-nitrile could be gained with high yields (Scheme 1 and Table 1). In our investigation, we found that the reaction could be finished within 10–15 min, Furthermore, the aromatic aldehydes, either bearing electron-withdrawing groups (such as halide) or electron-donating groups (such alkoxyl group), could be reacted smoothly in these process.

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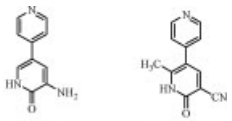

To examine the efficiency and the applicability of this process, then 3,4-dihydronaphthalen-1(2*H*)-one was chosen to react with aromatic aldehydes and malononitrile under same conditions. To our delight, the six-membered lactams, 4-aryl-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile was easily obtained with excellent yields, and these reactions could also be completed in a few minutes (about 10 min). Similarly, the aromatic aldehydes, bearing different groups, did not affect the reaction.

The structures of the products were confirmed on the basis of IR, ^{1}H NMR spectroscopic data, elemental analysis, and that of **4c** [10] and **4j** [11] was additionally confirmed by X-ray diffraction analysis (Figs. 1 and 2).

In conclusion, we have developed a rapid and highly efficient method for the synthesis of a variety of 4-aryl-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile and 4-aryl-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile derivatives *via* the reaction of different aromatic aldehydes, 2,3-dihydroinden-1-one or 3,4-dihydronaphthalen-1(2*H*)-one, and malononitrile under solvent-free conditions. The advantages of the present method in terms of avoiding to using toxic organic solvent, ease of manipulation, fast reaction rates, and lower cost should make this protocol as a valuable alternative to the existing methods.

EXPERIMENTAL

Melting points were determined on XT-5 microscopic melting-point apparatus and were uncorrected. IR spectra were recorded on a FT Bruker Tensor 27 spectrometer. ^{1}H NMR spectra were obtained from solution in DMSO-d_6 with Me_4Si as internal standard using a Bruker-400 spectrometer. Microanalyses were carried out using a Perkin–Elmer 2400 II analyzer. X-ray diffraction was measured on a Siemens P4 diffractometer.

The mixture of 2,3-dihydroinden-1-one or 3,4-dihydronaphthalen-1(2*H*)-one **1** (2 mmol), aromatic aldehydes **2** (2 mmol), malononitrile **3** (3 mmol), and NaOH (2 mmol) was put in a reaction flask and let them under 70°C about 10–15 min. After completing the reaction, the reaction mixture was poured into water, and then washed with water thoroughly. The product was filtered, dried, and recrystallized from 95% ethanol.

Scheme 1

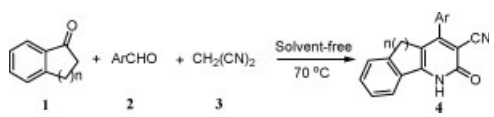

Table 1

Synthesis of product 4 under solvent-free conditions.

Entry	Ar[1]	Time (min)	*n*	Product	Yields
1	4-FC_6H_4	10	1	**4a**	88
2	4-BrC_6H_4	10	1	**4b**	89
3	4-ClC_6H_4	10	1	**4c**	95
4	2-ClC_6H_4	10	1	**4d**	90
5	2,4-$Cl_2C_6H_3$	10	1	**4e**	86
6	3,4-$Cl_2C_6H_3$	10	1	**4f**	88
7	4-$CH_3OC_6H_4$	15	1	**4g**	89
8	4-FC_6H_4	10	2	**4h**	91
9	4-BrC_6H_4	10	2	**4i**	93
10	4-ClC_6H_4	10	2	**4j**	92
11	2-ClC_6H_4	10	2	**4k**	89
12	3,4-$Cl_2C_6H_3$	10	2	**4l**	81
13	4-$CH_3C_6H_4$	15	2	**4m**	85
14	4-$CH_3OC_6H_4$	15	2	**4n**	89
15	3,4-$(CH_3)_2C_6H_3$	15	2	**4o**	86

4-(4-Fluorophenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4a). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3287, 3045, 2739, 2219, 1635, 1595, 1559, 1486, 1459, 1396, 1356, 1316, 1298, 1264, 1233, 1203, 1159, 1134, 1086, 1014, 955, 899, 835, 772, 734, 684, 634; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.67 (2H, s, CH_2), 7.52 (2H, t, J = 3.6 Hz, ArH), 7.62 (1H, d, J = 6.0 Hz, ArH), 7.68 (4H, q, J = 8.4 Hz, ArH), 7.16 (1H, d, J = 6.0 Hz, ArH), 13.65 (1H, s, NH). *Anal*. Calcd. For $C_{19}H_{11}FN_2O$: C 75.49, H 3.67, N 9.27. Found C 75.60, H 3.65, N 9.31.

4-(4-Bromophenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4b). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3241, 3016, 2790, 2222, 1636, 1592, 1564, 1486, 1460, 1387, 1354, 1316, 1297, 1271, 1227, 1202, 1161, 1130, 1067, 1010, 945, 898, 824, 768, 733, 674, 628; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.66 (2H, s, CH_2), 7.50–7.53 (2H, m, ArH), 7.63 (3H, t, J = 7.8 Hz, ArH), 7.70 (2H, d, J = 7.8 Hz, 8.4 Hz, ArH), 8.17 (1H, d, J = 2.0 Hz, ArH), 13.65 (1H, s, NH). *Anal*. Calcd. For $C_{19}H_{11}BrN_2O$: C 62.83, H 3.05, N 7.71. Found C 62.61, H 3.07, N 7.74.

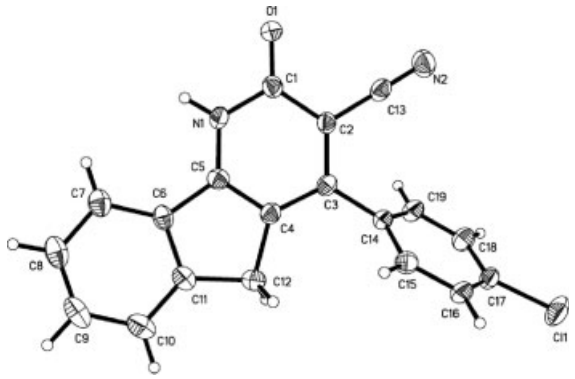

Figure 1. The structure of compound 4c.

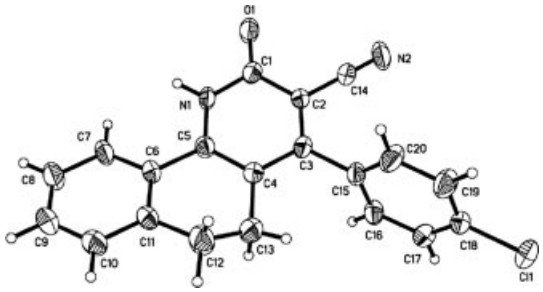

Figure 2. The structure of compound 4j.

4-(4-Chlorophenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4c). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3296, 3045, 2696, 2219, 1637, 1596, 1560, 1487, 1459, 1396, 1356, 1298, 1265, 1233, 1203, 1159, 1134, 1086, 1014, 955, 899, 835, 772, 734, 684, 634; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.68 (2H, s, CH_2), 7.53 (2H, t, J = 5.6 Hz, ArH), 7.64 (1H, d, J = 5.6 Hz, ArH), 7.70 (4H, dd, J = 8.4 Hz, 8.4 Hz, ArH), 8.19 (1H, d, J = 5.6 Hz, ArH), 13.68 (1H, s, NH). *Anal*. Calcd. For $C_{19}H_{11}ClN_2O$: C 71.59, H 3.48, N 8.79. Found C 71.41, H 3.50, N 8.84.

4-(2-Chlorophenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4d). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3337, 3066, 2222, 1698,1612, 1474, 1465, 1442, 1396, 1316, 1281, 1244, 1210, 1179, 1156, 1099, 1034, 1011, 918, 780, 758, 702, 667, 628; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.50 (2H, dd, J = 22.4 Hz, J = 22.4 Hz, CH_2), 7.54 (2H, t, J = 3.6 Hz, ArH), 7.58 (2H, br, ArH), 7.62 (2H, t, J = 4.0 Hz, ArH), 7.72 (1H, d, J = 7.2 Hz, ArH), 8.20 (1H, d, J = 4.0 Hz, ArH), 13.68 (1H, s, NH). *Anal*. Calcd. For $C_{19}H_{11}ClN_2O$: C 71.59, H 3.48, N 8.79. Found C 71.40, H 3.45, N 8.82.

4-(2,4-Dichlorophenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4e). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3291, 3067, 2781, 2223, 1635, 1594, 1561, 1482, 1458, 1419, 1399, 1375, 1351, 1315, 1298, 1272, 1255, 1202, 1190, 1155, 1135, 1010, 1056, 940, 900, 859, 838, 771, 735, 678, 652, 637; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 4.13 (2H, s, CH_2), 7.50–7.54 (1H, m, ArH), 7.52 (2H, t, J = 6.4 Hz, ArH), 7.84 (2H, t, J = 6.4 Hz, ArH), 7.89 (1H, d J = 6.8 Hz, ArH), 8.00 (1H, s, ArH), 13.85 (1H, s, NH). *Anal*. Calcd. For $C_{19}H_{10}Cl_2N_2O$: C 64.61, H 2.85, N 7.93. Found C 64.88, H 2.84, N 7.89.

4-(3,4-Dichlorophenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4f). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3339, 3072, 2744, 2219, 1658, 1616, 1558, 1507, 1488, 1481, 1458, 1419, 1398, 1375, 1355, 1299, 1268, 1229, 1203, 1191, 1139, 1122, 1032, 865, 824, 767, 728, 680, 669; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.71 (2H, s, CH_2), 7.54 (2H, q, J = 60 Hz, J = 7.2 Hz, ArH), 7.66 (1H, d, J = 7.2 Hz, ArH), 7.69 (1H, d, J = 8.4 Hz, ArH), 7.89 (1H, d J = 8.0 Hz, ArH), 8.04 (1H, d, J = 7.6 Hz, ArH), 8.19–8.21 (1H, br, ArH), 13.76 (1H, s, NH). *Anal*. Calcd. For $C_{19}H_{10}Cl_2N_2O$: C 64.61, H 2.85, N 7.93. Found C 64.50, H 2.87, N 7.90.

4-(4-Methoxyphenyl)-2-oxo-2,5-dihydro-1*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (4g). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3292, 3059, 2836, 2219, 1637, 1616, 1560, 1517, 1485, 1458, 1418, 1356, 1294, 1258, 1234, 1179, 1159, 1031, 835, 767, 731, 648; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.72 (2H, s, CH_2), 3.87 (3H, s, OCH_3), 7.14 (2H, t, J = 8.8 Hz, ArH), 7.52 (2H, t, J = 3.6 Hz, ArH), 7.66 (1H, m, ArH), 7.89 (2H, d, J = 8.8 Hz, ArH), 8.17 (1H, br, ArH), 13.59 (1H, s, NH). *Anal*. Calcd. For $C_{20}H_{14}N_2O_2$: C 76.42, H 4.49, N 8.91. Found C 76.60, H 4.47, N 8.87.

4-(4-Fluorophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile (4h). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3131, 3069, 2931, 2220, 1634, 1606, 1555, 1533, 1510, 1499, 1458, 1403, 1345, 1298, 1250, 1218, 1160, 1141, 1098, 894, 843, 824, 794, 772, 736; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.33 (2H, br, CH_2), 2.74 (2H, t, J = 7.2 Hz, CH_2), 7.35 (1H, d, J = 6.4 Hz, ArH), 7.39–7.46 (4H, m, ArH), 7.52 (2H, dd, J = 5.2 Hz, J = 5.6 Hz, ArH), 8.07 (1H, br, ArH), 12.77 (1H, s, NH). *Anal*. Calcd. For $C_{20}H_{13}FN_2O$: C 75.94, H 4.14, N 6.01. Found C 75.81, H 4.12, N 6.04.

4-(4-Bromophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile (4i). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3124, 3032, 2939, 2221, 1638, 1606, 1552, 1497, 1458, 1389, 1344, 1298, 1250, 1215, 1160, 1103, 1071, 1010, 908, 833, 811, 773, 738, 666; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.36 (2H, t, J = 6.0 Hz, CH_2), 2.76 (2H, t, J = 6.8 Hz, CH_2), 7.35 (1H, d, J = 6.8 Hz, ArH), 7.43 (4H, dd, J = 8.4 Hz, J = 8.4 Hz, ArH), 7.78 (2H, d, J = 8.8 Hz, ArH), 8.07 (1H, d, J = 7.6 Hz, ArH), 12.62 (1H, s, NH). *Anal*. Calcd. For $C_{20}H_{13}BrN_2O$: C 63.68, H 3.47, N 7.43. Found C 63.50, H 3.49, N 7.46.

4-(4-Chlorophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile (4j). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3130, 3031, 2931, 2223, 1637, 1553, 1535, 1498, 1460, 1425, 1340, 1346, 1297, 1251, 1217, 1198, 1176, 1142, 1086, 1014, 909, 836, 813, 774, 739, 707, 658; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.37 (2H, br, CH_2), 2.76 (2H, t, J = 6.8 Hz, CH_2), 7.35 (1H, d, J = 7.2 Hz, ArH), 7.43 (2H, dd, J = 7.2 Hz, J = 7.2 Hz, ArH), 7.49 (2H, d, J = 8.0 Hz, ArH), 7.64 (2H, d, J = 8.4 Hz, ArH), 8.07 (1H, d, J = 7.6 Hz, ArH), 12.62 (1H, s, NH). *Anal*. Calcd. For $C_{20}H_{13}ClN_2O$: C 72.18, H 3.94, N 8.42. Found C 72.38, H 3.91, N 8.46.

4-(2-Chlorophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile (4k). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3130, 3031, 2931, 2223, 1637, 1553, 1535, 1498, 1460, 1425, 1340, 1346, 1297, 1251, 1217, 1198, 1176, 1142, 1086, 1014, 909, 836, 813, 774, 739, 707, 658; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.37 (2H, br, CH_2), 2.76 (2H, t, J = 6.8 Hz, CH_2), 7.35 (1H, d, J = 7.2 Hz, ArH), 7.44 (4H, dd, J = 8.0 Hz, J = 8.0 Hz, ArH), 7.78 (2H, d, J = 8.4 Hz, ArH), 8.07 (1H, d, J = 7.6 Hz, ArH), 12.66 (1H, s, NH). *Anal*. Calcd. For $C_{20}H_{13}ClN_2O$: C 72.18, H 3.94, N 8.42. Found C 72.32, H 3.91, N 8.46.

4-(3,4-Dichlorophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]-quinoline-3-carbonitrile (4l). This compound was obtained as yellow crystals, mp 287–289°C; IR (KBr, ν, cm^{-1}): 3123, 3023, 2940, 2218, 1635, 1557, 1497, 1474, 1455, 1397, 1374, 1341, 1297, 1247, 1212, 1194, 1129, 1031, 952, 896, 821, 773, 737, 664; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.28 (1H, t, J = 7.2 Hz, CH_2), 2.38 (1H, t, J = 6.8 Hz, CH_2), 2.75 (2H, q, J = 6.8 Hz, J = 8.0 Hz, CH_2), 7.23–7.30 (1H, m, ArH), 7.35–7.48 (3H, m, ArH), 7.69–7.85 (2H, m, ArH), 8.03–

8.09 (1H, m, ArH), 12.54 (1H, s, NH). *Anal*. Calcd. For $C_{20}H_{12}Cl_2N_2O$: C 65.41, H 3.29, N 7.63. Found C 65.60, H 3.28, N 7.59.

2-Oxo-4-p-tolyl-1,2,5,6-tetrahydrobenzo[*h*]quinoline-3-carbonitrile e (4m). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3128, 3030, 2930, 2221, 1634, 1555, 1536, 1497, 1457, 1402, 1344, 1322, 1296, 1282, 1250, 1210, 1184, 1171, 1141, 1115, 1041, 1020, 975, 954, 905, 808, 774, 759, 737, 666; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.37 (2H, br, CH_2), 2.40 (3H, s, CH_3), 2.76 (2H, t, J = 7.2 Hz, CH_2), 7.31 (2H, d, J = 8.4 Hz, ArH), 7.36 (3H, d J = 8.4 Hz, ArH), 7.43 (2H, q, J = 6.4 Hz, J = 7.2 Hz, ArH), 8.07 (1H, d, J = 8.4 Hz, ArH), 12.65 (1H, s, NH). *Anal*. Calcd. For $C_{21}H_{16}N_2O$: C 80.75, H 5.16, N 8.97. Found C 80.55, H 5.19, N 8.92.

4-(4-Methoxyphenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]-quinoline-3-carbonitrile e (4n). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3120, 3032, 2936, 2219, 1636, 1556, 1515, 1497, 1457, 1398, 1341, 1295, 1255, 1212, 1180, 1142, 1025, 1020, 975, 838, 819, 772, 761, 736, 667; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.41 (2H, t, J = 6.0 Hz, CH_2), 2.75 (2H, t, J = 7.2 Hz, CH_2), 3.84 (3H, s, CH_3O), 7.11 (2H, d, J = 8.8 Hz, ArH), 7.34 (1H, d, J = 6.8 Hz, ArH), 7.38 (3H, d, J = 8.8 Hz, ArH), 7.43 (1H, t, J = 7.2 Hz, ArH), 8.06 (1H, d, J = 7.2 Hz, ArH), 12.58 (1H, s, NH). *Anal*. Calcd. For $C_{21}H_{16}N_2O_2$: C 76.81, H 4.91, N 8.53. Found C 76.62, H 4.88, N 8.56.

4-(3,4-Dimethylphenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[*h*]-quinoline-3-carbonitrile (4o). This compound was obtained as yellow crystals, mp >300°C; IR (KBr, ν, cm^{-1}): 3123, 3023, 2940, 2218, 1635, 1557, 1497, 1474, 1455, 1397, 1374, 1341, 1297, 1247, 1212, 1194, 1129, 1031, 952, 896, 821, 773, 737, 664; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.29 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.37 (2H, t, J = 7.2 Hz, CH_2), 2.73 (2H, t, J = 7.2 Hz, CH_2), 7.13 (1H, d, J = 7.6 Hz, ArH), 7.08 (1H, s, ArH), 7.32 (2H, t J = 7.6 Hz, ArH), 7.39 (1H, t, J = 7.6 Hz, ArH), 7.45 (1H, t, J = 7.6 Hz, ArH), 8.06 (1H, d, J = 7.6 Hz, ArH), 12.72 (1H, s, NH). *Anal*. Calcd. For $C_{22}H_{18}N_2O$: C 80.96, H 5.56, N 8.58. Found C 80.72, H 5.52, N 8.61.

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[10] X-ray crystallography for 4c: Empirical formula $C_{19}H_{11}ClN_2O$, F_w = 318.75, T = 298(2) K, triclinic, space group p −1, a = 7.163 (4) Å, b = 9.498(5) Å, c = 11.500(6) Å, α = 87.769(6)°, β = 79.052(7)°, γ = 80.758(7)°, V = 758.2(7) Å^3, Z = 2, Dcalcd. = 1.396 mg/m^3, λ(MoKα) = 0.71073 Å, μ = 0.257 mm^{-1}, F(000) = 328. 1.80° < θ < 25.00°, R = 0.0503, wR = 0.1008. s = 1.004. Largest diff. peak and hole: 0.234 and −0.330 e Å^{-3}.

[11] X-ray crystallography for 4j: Empirical formula $C_{20}H_{14}ClN_2O$, F_w = 333.78, T = 298(2) K, monoclinic, space group C2/c, a = 22.727 (11) Å, b = 8.399(4) Å, c = 18.035(9) Å, α = 90°, β = 107.651(7)°, γ = 90°, V = 3281(3) Å^3, Z = 8, Dcalcd. = 1.352 mg/m^3, λ(MoKα) = 0.71073 Å, μ = 0.241 mm^{-1}, F(000) = 1384. 1.88° < θ < 25.00°, R = 0.0758, wR = 0.1783. s = 1.043. Largest diff. peak and hole: 0.280 and −0.433 e Å^{-3}.