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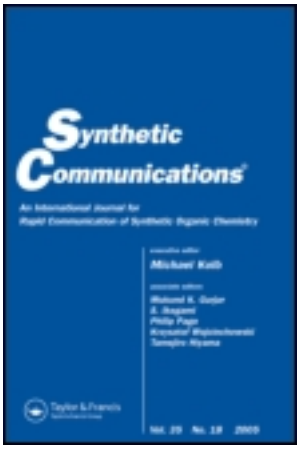

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Efficient NaOH-Catalyzed Reaction of Aromatic Aldehyde, Cyclic Ketones, and Malononitrile Under Solvent-Free Conditions Using a Grinding Method

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Published online: 29 Sep 2008.

To cite this article: Liangce Rong , Hongxia Han , Hong Jiang & Shujiang Tu (2008): Efficient NaOH-Catalyzed Reaction of Aromatic Aldehyde, Cyclic Ketones, and Malononitrile Under Solvent-Free Conditions Using a Grinding Method, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 38:20, 3530-3542

To link to this article: http://dx.doi.org/10.1080/00397910802164724

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Synthetic Communications®, 38: 3530–3542, 2008
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802164724

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Efficient NaOH-Catalyzed Reaction of Aromatic Aldehyde, Cyclic Ketones, and Malononitrile Under Solvent-Free Conditions Using a Grinding Method

Liangce Rong,[1,2] Hongxia Han,[1] Hong Jiang,[2] and Shujiang Tu[1,2]
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Abstract: An efficient and facile synthesis of 2,6-dicyanoanilines via a one-pot reaction of aromatic aldehydes, malononitrile, and cyclic ketones in the presence of NaOH under solvent-free conditions using a grinding method has been developed. Compared with the classical reaction conditions, the new synthetic method has the advantages of excellent yields, shorter reaction times, and mild reaction conditions.

Keywords: 2,6-Dicyanoanilines, green chemistry, grinding, solvent free, synthesis

Developing green organic syntheses is very important now. Organic synthesis in the absence of solvent is a powerful tool for the generation of structurally diverse molecules, and it is attractive because of reduced pollution, low costs, mild reaction conditions, easy separation, and easy purification. Therefore, in recent years, solvent-free organic reactions have attracted great interest.[1] Many reactions proceed efficiently without solvent. Indeed, in many cases, the solvent-free organic reaction occurs more efficiently and more selectively than does its solution counterpart, because molecules in a solid state are arranged tightly and regularly. Some solvent-free reactions can be carried out just by grinding.[2]

Received February 2, 2008.
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Currently, solvent-free organic reactions have attracted much interest not only for laboratory synthesis but also in the chemical industry.

2,6-Dicyanoanilines are typical acceptor–donor–acceptor (A-D-A) systems comprising one electron donor and two electron acceptors,[3,4] which are very important compounds for their optical properties[5] and are the basis for artificial photosynthetic systems,[6,7] materials presenting semiconducting or nonlinear optical properties,[8] and molecular electronic devices.[9] The synthesis of these compounds has attracted attention of chemists. Though several methods for their synthesis have been reported,[10–13] many of these procedures are not fully satisfactory with regard to operational simplicity, cost of the reagent, and isolated yield; moreover, the majority of those synthetic methods were carried out in nocuous organic solvent.

In continuation of our current studies on the application of solvent-free conditions for the synthesis of organic compounds,[14–17] herein, we report a practical and simple method to prepare polysubstituted 2,6-dicyanoaniline derivatives by grinding the starting materials under dry conditions at room temperatures.

In an initial endeavor, 4-methylbenzaldehyde and cyclohexanone were chosen to react with malononitrile as a model reaction in the presence of different catalysts. We found when weak bases (K_2CO_3, Al_2O_3) or acidic catalysts [H_2SO_4, $B(OH)_3$] were used, the reaction could not be carried out. However, when a strong base, such as NaOH was used, the reacion could be carried out smoothly. The other stronger base, KOH, also could promote the reaction, but it did not improve the yield more than NaOH

Table 1. Synthesis of **3a** under solvent-free conditions in the presence of different catalysts[a]

Entry	Amount (g)	Catalyst	Yield[b] (%)
1	1	$ZnCl_2$	0
2	1	$B(OH)_3$	0
3	1	H_2SO_4	0
4	2	Na_2CO_3	0
5	2	K_2CO_3	0
6	3	Al_2O_3[c]	0
7	2	$Ba(OH)_2$	30
8	0.2	NaOH	63
9	0.2	KOH	60

[a]Reagents and conditions: 4-methylbenzaldehyde **1** (2 mmol), malononitrile **2** (5 mmol), cyclohexanone **3** (2 mmol), and NaOH (0.2 g).

[b]Isolated yields.

[c]Basic.

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Table 2. Optimizing the reaction conditions[a]

Entry	Amount (g)	Time (min)	Yield[b] (%)
1	0.1	10	40
2	0.2	3	63
3	0.3	5	50
4	0.4	5	48

[a]Reagents and conditions: 4-methylbenzaldehyde **1** (2 mmol), malononitrile **2** (5 mmol).
[b]Isolated yields.

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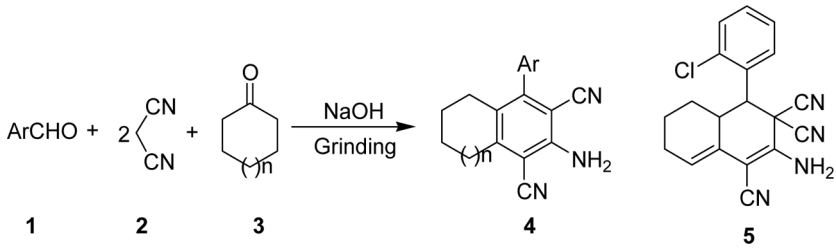
did. The results are listed in Table 1. Among these catalysts, NaOH was the most efficient catalyst of choice in terms of yields and cost.

With this optimistic result in hand, we further investigated the best reaction conditions. We investigated the reaction outcome using different amounts of NaOH. To increase the quantity of NaOH from 0.1 to 0.4 g, the reaction gave different outcomes, resulting in the isolation of **3a** in about 40, 63, 50, and 48% yields, respectively. Higher loading of the catalyst did not improve the yields of the reaction. Perhaps more NaOH could turn the reagents into solid more quickly, which hindered the reaction from completion. The results of the reaction are listed in Table 2. As shown in Table 2, the best amount of NaOH was 0.2 g.

Using this condition, a series of 2,6-dicyanoaniline derivatives was synthesized from aromatic aldehyde, malononitrile, and cyclohexanone or cyclopentanone (Scheme 1). The results are summarized in Table 3. From Table 3, we find that the aldehydes bearing either electron-with drawing or electron-donating groups perform well in this reaction. Therefore, we concluded that the electronic nature of the substituents has no significant effect on this reaction.



Scheme 1. The reactions of aromatic aldehyde, cyclic ketones, and malonitrile under solvent-free conditions.

Table 3. Synthetic results of compounds 4

Entry	Ar	n	Time (min)	Product	Yield (%)
1	4-$CH_3C_6H_4$	1	3	**4a**	63
2	3,4-$Cl_2C_6H_3$	1	2	**4b**	66
3	4-$CH_3OC_6H_4$	1	2	**4c**	71
4	2-ClC_6H_4	1	2	**4d**	68
5	2,4-$Cl_2C_6H_3$	1	2	**4e**	67
6	3,4-$(CH_3)_2C_6H_3$	1	3	**4f**	60
7	3,4-$(CH_3O)_2C_6H_3$	1	3	**4g**	58
8	4-FC_6H_4	1	2	**4h**	73
9	4-$CH_3C_6H_4$	0	2	**4i**	71
10	2-ClC_6H_4	0	2	**4j**	72
11	4-ClC_6H_4	0	2	**4k**	70
12	3-ClC_6H_4	0	2	**4l**	70
13	2,4-$Cl_2C_6H_3$	0	2	**4m**	72
14	3,4-$Cl_2C_6H_3$	0	2	**4n**	68
15	3,4-$(CH_3)_2C_6H_3$	0	2	**4o**	63
16	4-$CH_3OC_6H_4$	0	2	**4p**	65

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According to the product, the possible mechanism could be explained by Scheme 2. To our delight, we obtained the intermediate **5** of product **4d**. X-ray diffraction analysis of the intermediate **5** confirmed our conjecture.

The structures of **4** were characterized by ^{1}H NMR, IR, and elemental analysis, and the structures of **4a** and the intermediate **5** were

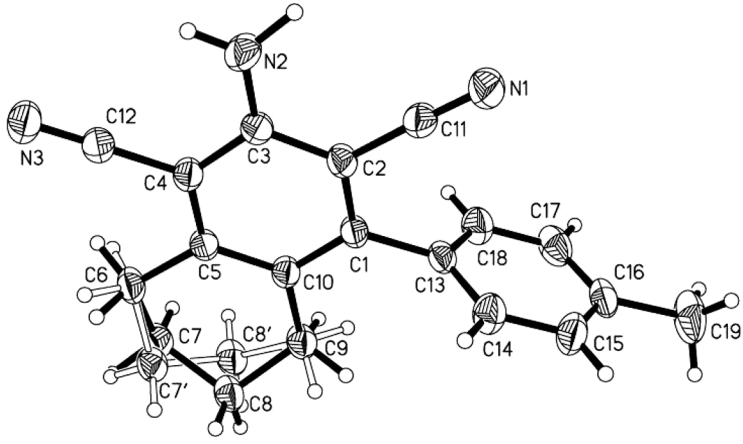

Figure 1. Structure of compound **4a**.

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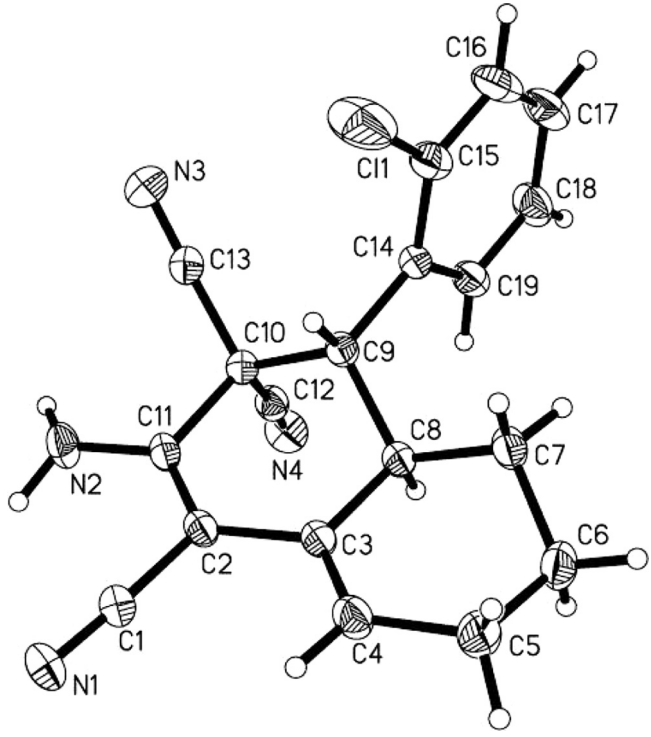
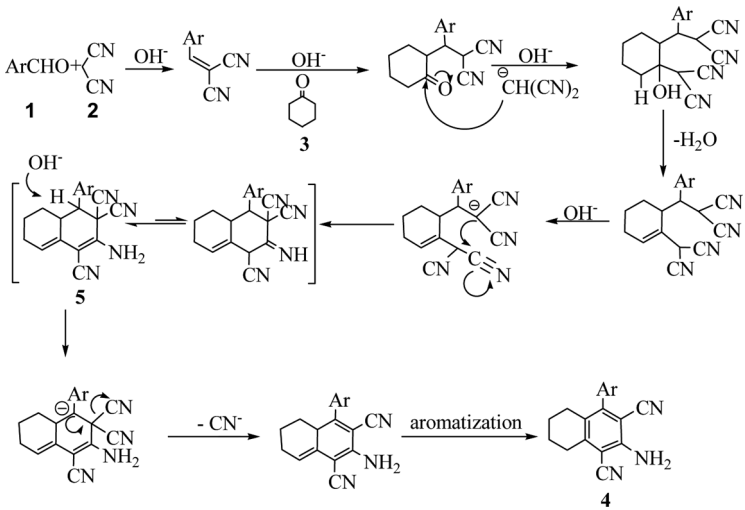


Figure 2. Structure of compound **5**.



Scheme 2. Mechanisms of the reaction.

additionally confirmed by X-ray diffraction analysis. The crystal structures of **4a** and **5** are shown in Figs. 1 and 2, respectively.

In conclusion, we have successfully developed an efficient and facile method to prepare a variety of polysubstituted 2,6-dicyanoaniline derivatives via the one-pot reaction of different aromatic aldehydes, cyclic ketones, and malononitrile under solvent-free conditions. We found that NaOH was an excellent catalyst, because the reaction completed within 2–3 min. The important intermediate **5** was obtained successfully to confirm the presented mechanism. Because no toxic organic solvent was used, this new protocol has the advantages of good yields, lower cost, reduced environmental impact, and convenient procedure.

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EXPERIMENTAL

General Procedure

Melting points were uncorrected. IR spectra were recorded on a Tensor 27 spectrometer in KBr. ^{1}H NMR spectra were obtained in DMSO-d_6 solution with Me_4Si as internal standard using a Bruker-400 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 240 II analyzer. X-ray diffractions were recorded on a Siemens P4 or Simart-1000 diffractometer.

General Procedure for the Syntheses of 2,6-Dicyanoaniline Derivatives

The general procedure is represented as follows: aromatic aldehyde **1** (2 mmol), malononitrile **2** (5 mmol), ketone **3** (2 mmol), and NaOH (0.2 g) were added to a mortar. The mixture was ground with a pestle at room temperature. The reaction was completed within 2–3 min, and the reaction mixture was poured into water. The product was filtered, dried, and recrystallized from 95% ethanol.

Data

2-Amino-5,6,7,8-tetrahydro-4-*p*-tolylnaphthalene-1,3-dicarbonitrile (**4a**)

Mp: 189–191°C. IR (KBr) *v*: 3443, 3357, 3250, 2958, 2873, 2220, 2210, 1648, 1566, 1518, 1458, 1436, 1318, 1269, 1171, 1021, 850, 816, 737 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.55 (2H, t, $J = 5.6$ Hz, CH_2), 1.71 (2H, t, $J = 5.6$ Hz, CH_2), 2.16 (2H, t, $J = 6.0$ Hz, CH_2), 2.38 (3H, s, CH_3), 2.84 (2H, t, $J = 6.0$ Hz, CH_2), 6.43 (2H, s, NH_2), 7.15 (2H, d, $J = 8.0$ Hz, ArH), 7.31 (2H, d, $J = 8.0$ Hz, ArH). Anal.

calcd. for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.49; H, 5.93; N, 14.69.

2-Amino-4-(3,4-dichlorophenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4b**)

Mp: 229–230 °C. IR (KBr) *v*: 3415, 3345, 3249, 2939, 2864, 2216, 1655, 1563, 1477, 1460, 1327, 1281, 1269, 1170, 1128, 1032, 888, 824, 816, 737 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.59 (2H, t, $J = 6.4$ Hz, CH_2), 1.72 (2H, t, $J = 6.4$ Hz, CH_2), 2.17 (2H, t, $J = 6.0$ Hz, CH_2), 2.86 (2H, t, $J = 6.0$ Hz, CH_2), 6.51 (2H, s, NH_2), 7.31–7.34 (1H, dd, $J = 2.0$ Hz, $J = 2.0$ Hz, ArH), 7.67 (1H, d, $J = 2.0$ Hz, ArH), 7.78 (1H, d, $J = 8.4$ Hz, ArH). Anal. calcd. for $C_{18}H_{13}Cl_2N_3$: C, 63.17; H, 3.83; N, 12.28. Found: C, 63.25; H, 3.75; N, 12.39.

2-Amino-4-(4-methoxyphenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4c**)

Mp: 192–194 °C. IR (KBr) *v*: 3417, 3352, 2934, 2838, 2214, 1654, 1608, 1559, 1516, 1455, 1420, 1293, 1279, 1255, 1175, 1030, 824, 804 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.56 (2H, t, $J = 6.0$ Hz, CH_2), 1.72 (2H, t, $J = 6.0$ Hz, CH_2), 2.19 (2H, t, $J = 6.4$ Hz, CH_2), 2.84 (2H, t, $J = 6.4$ Hz, CH_2), 3.82 (3H, s, OCH_3), 6.40 (2H, s, NH_2), 7.05 (2H, d, $J = 8.4$ Hz, ArH), 7.21 (2H, d, $J = 8.8$ Hz, ArH). Anal. calcd. for $C_{19}H_{17}N_3O$: C, 75.23; H, 5.65; N, 13.85. Found: C, 75.16; H, 5.76; N, 13.79.

2-Amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4d**)

Mp: 201–203 °C. IR (KBr) *v*: 3413, 3345, 3249, 2936, 2863, 2216, 1655, 1562, 1461, 1406, 1282, 1255, 1171, 1090, 1078, 880, 807, 788, 731, 717 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.59 (2H, t, $J = 6.4$ Hz, CH_2), 1.69 (2H, t, $J = 6.4$ Hz, CH_2), 2.16 (2H, t, $J = 6.0$ Hz, CH_2), 2.85 (2H, t, $J = 6.0$ Hz, CH_2), 6.51 (2H, s, NH_2), 7.25?7.27 (1H, m, ArH), 7.42 (1H, d, $J = 0.8$ Hz, ArH), 7.54 (2H, d, $J = 8.0$ Hz, ArH). Anal. calcd. for $C_{18}H_{14}ClN_3$: C, 70.24; H, 4.58; N, 13.65. Found: C, 70.16; H, 4.64; N, 13.77.

2-Amino-4-(2,4-dichlorophenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4e**)

Mp: 185–187 °C. IR (KBr) *v*: 3451, 3348, 3245, 2952, 2863, 2226, 2213, 1645, 1589, 1563, 1481, 1458, 1435, 1381, 1276, 1170, 1104, 1056, 885,

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818, 752 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.59 (2H, t, $J = 6.0$ Hz, CH_2), 1.72 (2H, t, $J = 6.0$ Hz, CH_2), 2.18 (2H, t, $J = 6.4$ Hz, CH_2), 2.85 (2H, t, $J = 6.4$ Hz, CH_2), 6.60 (2H, s, NH_2), 7.40 (1H, d, $J = 8.4$ Hz, ArH), 7.59?7.61 (1H, dd, $J = 2.0$ Hz, $J = 1.6$ Hz, ArH), 7.86 (1H, d, $J = 2.0$ Hz, ArH). Anal. calcd for $C_{18}H_{13}Cl_2N_3$: C, 63.17; H, 3.83; N, 12.28. Found: C, 63.23; H, 3.76; N, 12.17.

2-Amino-4-(3,4-dimethylphenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4f**)

Mp: 210–212 °C. IR (KBr) *v*: 3464, 3359, 3238, 2941, 2865, 2213, 1636, 1565, 1505, 1454, 1282, 1262, 1172, 1125, 1031, 816, 734 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.55 (2H, t, $J = 2.4$ Hz, CH_2), 1.681.74 (2H, m, CH_2), 2.09–2.18 (2H, m, CH_2), 2.26 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.83 (2H, t, $J = 6.4$ Hz, CH_2), 6.40 (2H, s, NH_2), 6.96 (1H, d, $J = 7.6$ Hz, ArH), 7.03 (1H, s, ArH), 7.25 (1H, d, $J = 7.6$ Hz, ArH). Anal. calcd. for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.77; H, 6.29; N, 13.85.

2-Amino-4-(3,4-dimethoxyphenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4g**)

Mp: 223–225 °C. IR (KBr) *v*: 3428, 3349, 3247, 2965, 2924, 2863, 2838, 2213, 1644, 1566, 1516, 1456, 1436, 1319, 1255, 1172, 1143, 1027, 819, 735 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.56 (2H, t, $J = 6.0$ Hz, CH_2), 1.72 (2H, t, $J = 6.0$ Hz, CH_2), 2.25 (2H, t, $J = 6.0$ Hz, CH_2), 2.85 (2H, t, $J = 6.4$ Hz, CH_2), 3.75 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.40 (2H, s, NH_2), 6.80 (1H, d, $J = 8.0$ Hz, ArH), 6.86 (1H, d, $J = 1.2$ Hz, ArH), 7.06 (1H, d, $J = 8.4$ Hz, ArH). Anal. calcd. for $C_{20}H_{19}N_3$: C, 72.05; H, 5.74; N, 12.60. Found: C, 72.13; H, 5.65; N, 12.71.

2-Amino-4-(4-fluorophenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (**4h**)

Mp: 255–256 °C. IR (KBr) *v*: 3420, 3342, 3255, 3232, 2951, 2873, 2212, 1649, 1605, 1511, 1456, 1392, 1272, 1231, 1165, 845, 808, 755 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.56 (2H, t, $J = 6.0$ Hz, CH_2), 1.72 (2H, t, $J = 6.0$ Hz, CH_2), 2.15 (2H, t, $J = 6.4$ Hz, CH_2), 2.84 (2H, t, $J = 6.4$ Hz, CH_2), 6.47 (2H, s, NH_2), 7.35 (4H, d, $J = 7.2$ Hz, ArH). Anal.

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calcd. for $C_{18}H_{14}FN_3$: C, 74.21; H, 4.84; N, 14.42. Found: C, 74.13; H, 4.91; N, 14.31.

5-Amino-2,3-dihydro-7-*p*-tolyl-1*H*-indene-4,6-dicarbonitrile (**4i**)

Mp: 181–182 °C. R (KBr) *v*: 3409, 3350, 3252, 2957, 2217, 1655, 1571, 1516, 1459, 1403, 1366, 1319, 1305, 1265, 1180, 1119, 1021, 815, 745 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.99 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.38 (3H, s, CH_3), 2.62 (2H, t, $J = 7.6$ Hz, CH_2), 2.99 (2H, t, $J = 7.2$ Hz, CH_2), 6.53 (2H, s, NH_2), 7.31 (4H, s, ArH). Anal. calcd. for $C_{18}H_{15}N_3$: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.21; H, 5.41; N, 15.31.

5-Amino-7-(2-chlorophenyl)-2,3-dihydro-1*H*-indene-4,6-dicarbonitrile (**4j**)

Mp: 162–164 °C. IR (KBr) *v*: 3417, 3352, 3251, 2955, 2221, 1654, 1637, 1573, 1507, 1460, 1420, 1369, 1319, 1304, 1268, 1211, 1054, 1031, 771, 746 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.02 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.45 (2H, t, $J = 7.6$ Hz, CH_2), 3.04 (2H, t, $J = 7.2$ Hz, CH_2), 6.67 (2H, s, NH_2), 7.38–7.40 (1H, m, ArH), 7.47–7.54 (2H, m, ArH), 7.63–7.66 (1H, m, ArH). Anal. calcd. for $C_{17}H_{12}ClN_3$: C, 69.51; H, 4.12; N, 14.30. Found: C, 69.45; H, 4.19; N, 14.22.

5-Amino-7-(4-chlorophenyl)-2,3-dihydro-1*H*-indene-4,6-dicarbonitrile (**4k**)

Mp: 152–154 °C. IR (KBr) *v*: 3417, 3350, 3251, 2954, 2220, 1653, 1573, 1460, 1434, 1419, 1319, 1305, 1268, 1055, 1031, 770, 745 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.01 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.45 (2H, t, $J = 7.6$ Hz, CH_2), 3.04 (2H, t, $J = 7.2$ Hz, CH_2), 6.67 (2H, s, NH_2), 7.40 (1H, d, $J = 8.0$ Hz, ArH), 7.45–7.63 (2H, m, ArH), 7.64 (1H, d, $J = 8.0$ Hz, ArH). Anal. calcd. for $C_{17}H_{12}ClN_3$: C, 69.51; H, 4.12; N, 14.30. Found: C, 69.56; H, 4.07; N, 14.39.

5-Amino-7-(3-chlorophenyl)-2,3-dihydro-1*H*-indene-4,6-dicarbonitrile (**4l**)

Mp: 161–165 °C. IR (KBr) *v*: 3409, 3347, 3249, 2958, 2213, 1653, 1567, 1481, 1457, 1406, 1319, 1305, 1274, 1260, 1694, 1080, 882, 793, 745, 693 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.00 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.61 (2H, t, $J = 7.6$ Hz, CH_2), 3.02 (2H, t,

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$J = 7.2$ Hz, CH_2), 6.64 (2H, s, NH_2), 7.38–7.43 (1H, m, ArH), 7.47–7.58 (3H, m, ArH). Anal. calcd. for $C_{17}H_{12}ClN_3$: C, 69.51; H, 4.12; N, 14.30. Found: C, 69.58; H, 4.19; N, 14.26.

5-Amino-7-(2,4-dichlorophenyl)-2,3-dihydro-1*H*-indene-4,6-dicarbonitrile (**4m**)

Mp: 201–203 °C. IR (KBr) *v*: 3421, 3347, 3251, 2965, 2216, 1652, 1590, 1751, 1485, 1460, 1419, 1385, 1271, 1255, 1104, 1055, 893, 819, 780 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.01 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.46 (2H, t, $J = 7.2$ Hz, CH_2), 3.04 (2H, t, $J = 7.6$ Hz, CH_2), 6.72 (2H, s, NH_2), 7.45 (1H, d, $J = 8.0$ Hz, ArH), 7.58–7.60 (1H, dd, $J_1 = 2.0$ Hz, $J_2 = 2.0$ Hz, ArH), 7.85 (1H, d, $J = 2.0$ Hz, Hz, ArH). Anal. calcd. for $C_{17}H_{11}Cl_2N_3$: C, 62.21; H, 3.38; N, 12.80. Found: C, 62.30; H, 3.30; N, 12.88.

5-Amino-7-(3,4-dichlorophenyl)-2,3-dihydro-1*H*-indene-4,6-dicarbonitrile (**4n**)

Mp: 257–259 °C; IR (KBr) *v*: 3461, 3359, 3233, 2919, 2215, 1626, 1564, 1543, 1473, 1455, 1436, 1373, 1315, 1282, 1249, 1132, 1030, 894, 756 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.95–2.09 (2H, m, CH_2), 2.62–2.2.69 (2H, m, CH_2), 2.93–3.10 (2H, m, CH_2), 6.78 (2H, s, NH_2), 7.48–7.52 (1H, m, ArH), 7.67–7.75 (1H, m, ArH), 7.81–7.85 (1H, m, ArH). Anal. calcd for $C_{17}H_{11}Cl_2N_3$: C, 62.21; H, 3.38; N, 12.80. Found: C, 62.38; H, 3.45; N, 12.73.

5-Amino-7-(3,4-dimethylphenyl)-2,3-dihydro-1*H*-indene-4,6-dicarbonitrile (**4o**)

Mp: 140–142 °C. IR (KBr) *v*: 3416, 3350, 3251, 2945, 2918, 2216, 1655, 1571, 1505, 1458, 1383, 1379, 1318, 1305, 1267, 1125, 1018, 823, 749 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.98 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.27 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.61 (2H, t, $J = 7.2$ Hz, CH_2), 3.00 (2H, t, $J = 7.6$ Hz, CH_2), 6.54 (2H, s, NH_2), 7.12 (1H, d, $J = 7.8$ Hz, ArH), 7.18 (1H, s, ArH), 7.25 (1H, d, $J = 8.0$ Hz, ArH). Anal. calcd. for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.48; H, 5.89; N, 14.73.

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5-Amino-2,3-dihydro-7-(4-methoxyphenyl)-1*H*-indene-4,6-dicarbonitrile (**4p**)

Mp: 189–191 °C. IR (KBr) *v*: 3403, 3345, 3249, 2967, 2936, 2217, 1655, 1609, 1565, 1517, 1458, 1408, 1365, 1318, 1294, 1254, 1176, 1032, 838, 761 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.99 (2H, q, $J = 7.2$ Hz, 7.6 Hz, CH_2), 2.64 (2H, t, $J = 7.6$ Hz, CH_2), 3.00 (2H, t, $J = 7.2$ Hz, CH_2), 3.82 (3H, s, OCH_3), 6.52 (2H, s, NH_2), 7.06 (2H, d, $J = 8.4$ Hz, ArH), 7.37 (2H, d, $J = 8.4$ Hz, ArH). Anal. calcd. for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.58; H, 5.32; N 14.63.

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X-ray Crystallography for 4a

Empirical formula $C_{19}H_{17}N_3$, $Fw = 287.36$, $T = 294(2)$ K, monclinic, space group $C2/c$, $a = 22.837$ (6); $b = 7.906(2)$, $c = 17.920(4)$, $\alpha = 90°$, $\beta = 105.995(5)°$, $\gamma = 90°$, $V = 3110.8(14)^3$, $Z = 8$, $Dc = 1.227$ Mg/m^3, λ (MoKα) = 0.71073, $\mu = 0.074$ mm^{-1}, $F(000) = 1216$. $2.36° < \theta < 25.00°$, $R = 0.0492$, w$R = 0.1184$, S = 0.999. Largest diff. peak and hole: 0.184 and -0.159 e^{-3}.

X-Ray Crystallography for 5

Empirical formula $C_{19}H_{15}ClN_4$, $Fw = 334.8$, $T = 294(2)$ K, monoclinic, space group $p\ 2(1)/c$, $a = 13.0487$ (18), $b = 9.1339$ (12), $c = 13.9867$ (19), $\alpha = 90°$, $\beta = 90.124(2)°$, $\gamma = 90°$, $V = 1667.0$ $(4)^3$, $Z = 4$, $Dc = 1.334$ Mg/m^3, λ (MoKα) = 0.71073; $\mu = 0.236$ mm^{-1}, $F(000) = 696$, $1.56° < \theta < 26.43°$, $R = 0.0394$, $wR = 0.0913$, $S = 1.034$. Largest diff. peak and hole: 0.227 and -0.268 e^{-3}.

ACKNOWLEDGMENTS

We thank the PeiYu Foundation (07PYL06) of Xuzhou Normal University for financial support.

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