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# Microwave-Assisted One-Pot Synthesis of 3-Amino-1-aryl-8-bromo-2,4-dicyano-9H-fluorenes in Water

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#### MICROWAVE-ASSISTED ONE-POT SYNTHESIS OF 3-AMINO-1-ARYL-8-BROMO-2,4-DICYANO-9*H*-FLUORENES IN WATER

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#### **GRAPHICAL ABSTRACT**



**Abstract** A series of novel 3-amino-1-aryl-8-bromo -2,4-dicyano-9H-fluorenes derivatives were prepared using arylaldehyde, 4-bromo-indanone, malononitrile, and sodium hydroxide as the reactants in water via one-pot synthesis under microwave irradiation. A green and efficient method was successfully developed via microwave irradiation. The method possesses several advantages, such as environmental friendliness, shorter reaction time, and simple workup procedure.

Keywords Fluorene; microwave irradiation; synthesis; water

#### INTRODUCTION

In recent years, microwave-assisted organic synthesis as a green method has become an important research field.<sup>[1–7]</sup> Compared with other expensive toxic organic solvents, the inexpensive and pollution-free aqueous medium has been eagerly applied in microwave irradiation.<sup>[8–10]</sup> Moreover, the water as solvent provides us with a convenient way to separate the product from the reaction system.

3-Amino-1-aryl-2,4-dicyano-9*H*-fluorenes are typical acceptor-donor-acceptor (A-D-A) systems, which have been found exhibit strong fluorescence in previous studies.<sup>[11,12]</sup> A-D-A systems comprise one electron donor and two electron acceptors in the extensive study of photo-induced intramolecular electron transfer,<sup>[13,14]</sup> which has potential applications in electron devices such as light-emitting diodes<sup>[15,16]</sup> and field-effect transistors.<sup>[17]</sup> Besides, 9*H*-fluorene derivatives have a strong inhibitory effect on cholesterol biosynthesis<sup>[18]</sup> and anti-inflammatory activity.<sup>[19]</sup>

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Scheme 1. Synthesis of 4 in water under MWI.

Many synthetic methods for the preparation of 2,4-dicyano-9*H*-fluorenes have been reported.<sup>[20-22]</sup> However, some methods need longer reaction time, more complex original materials, organic base catalyst, and organic solvent. Keeping in view the importance of 3-amino-1-aryl-2,4-dicyano-9*H*-fluorenes and recent trends of using of environmentally friendly techniques, a green method to synthesize a series of new 3-amino-1-aryl-8-bromo-2,4-dicyano-9*H*-fluorenes **4** in water was developed under microwave irradiation (MWI) from arylaldehyde **1**, 4-bromo-indan-1-one **2**, malononitrile **3**, and sodium hydroxide (Scheme 1). To optimize the reaction condition, a comparison was done between MWI and conventional heating.

#### **RESULTS AND DISCUSSION**

To optimize the reaction conditions, the effects of different reaction time and MWI power were investigated in the synthesis of 4a. The reactions of benzaldehyde 1a (2 mmol), 4-bromo-indan-1-one 2 (2 mmol), malononitrile 3 (4.5 mmol), and sodium hydroxide (5 mmol) were carried out in water at 100 °C. The results showed that the yield of product 4a was improved as the MWI time was increased from 3 to 7 min in an increment of 2 min each time. However, as the reaction time increased continuously, the yield of the products was decreasing. Therefore, 7 min was chosen for all the further reactions (Fig. 1).

The MWI power was optimized by carrying out the experiment at 250 to 450 W in increments of 50 W, and the reaction time and temperature was 7 min and  $100 \,^{\circ}$ C respectively. The results showed that MWI at 400 W gave the best yield (Fig. 2).

Furthermore, we tested the same reaction in different solvents under the optimized reaction conditions, namely, 100 °C at MWI power of 400 W for 7 min (Table 1). We found that the reaction carried out in water gave the greatest yield. Considering the nontoxic and inexpensive character of water, we chose water as the optimum solvent.

Under these reaction conditions, we synthesized a series of products of 3-amino-1-aryl-8-bromo-2,4-dicyano-9*H*-fluorenes **4** (Table 2).

We performed the synthesis of **4** under both MWI and classical heating conditions. Compared with the 6–7 h reaction using conventional heating, little time was needed under MWI. Moreover, a greater yield was obtained when we performed the reaction using MWI (Table 3). Therefore, MWI exhibited several advantages over classical heating.



Figure 1. Effect of MWI time on the yield of 4a.



Figure 2. Effect of MWI power on the yield of 4a.

Table 1. Investigation of solvent in the synthesis of 4a (C<sub>6</sub>H<sub>5</sub>)

Entry	Solvent	Time (min)	Yield (%)	
1	MeOH	6	67.8	
2	EtOH	7	56.3	
3	$H_2O$	7	74.4	
4	$EtOH/H_2O=1{:}1$	7	64.5	

*Note.* The product **4a** was synthesized under MWI at  $100 \,^{\circ}$ C and the MWI power was 400 W.

Compound	Ar	М	Mp (°C)	Yield (%)
4a	C <sub>6</sub> H <sub>5</sub>	$C_{21}H_{12}BrN_3$	268-270	74.4
4b	3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	$C_{22}H_{14}BrN_3$	299-300	54.4
4c	$2-C_4H_3O$	$C_{19}H_{10}BrN_3O$	234-236	77.2
4d	$1 - C_{10}H_7$	$C_{25}H_{14}BrN_3$	298-300	69.7
4e	$2-C_4H_3S$	$C_{19}H_{10}BrN_3S$	223-225	81.6
4f	$4-C_5H_4N$	$C_{20}H_{11}BrN_4$	301-303	48.7
4g	$3,4-(F)_2C_6H_3$	$C_{21}H_{10}BrF_2N_3$	224-226	89.0
4h	$3-FC_6H_4$	$C_{21}H_{11}BrFN_3$	289–291	52.1

Table 2. Synthesis of 4 in water under MWI

Table 3. Comparison of reaction times and yields for compounds 4 using microwave and classical methods

Compound	Reaction time		Yield (%)	
	Microwave (min)	Classical heating (h)	Microwave	Classical heating
4a	7	6	74.4	68.4
4b	7	6	54.4	45.9
4c	6	6	77.2	54.0
4d	7	6	69.7	63.1
<b>4</b> e	7	6	81.6	74.9
4f	7	6	48.7	41.5
4g	6	6.5	89.0	72.8
4h	7	6.5	52.1	46.6

The reaction was assumed to proceed via a mechanism of Knoevenagel condensation, Michael addition, cyclization, and elimination. Aldehyde 1 and ketone 2 reacted with malononitrile in the presence of a base to give 2-arylidenemalonodinitriles 5 and 2-(4-bromo-2,3-dihydroinden-1-ylidene)malononitrile 6, and Michael addition reaction of 6 and 5 afforded intermediate 7, which undergoes intramolecular cyclization, isomerization, and elimination to finally afford 3-amino-1-aryl-8-bromo-2,4-dicyano-9*H*-fluorenes 4 (Scheme 2).



Scheme 2. Mechanisms of the reaction.



Figure 3. Crystal structure of the product 4a.

All the structures of the products were confirmed by means of Fourier transform infrared (FTIR) and<sup>1</sup>H NMR analysis. Furthermore, the structure of **4a** was established by the x-ray crystallographic analysis (Fig. 3).

In conclusion, we developed a green method for the synthesis of 3-amino-1aryl-8-bromo-2,4-dicyano-9*H*-fluorenes using an inexpensive original material under MWI and got a series of new products, some of which were never reported in literature. Above all, the use of water leads to a new and nontoxic method for the organic reaction.

#### EXPERIMENTAL

The melting points were determined on an X-4 microscopic melting-point apparatus and are uncorrected. The reactions were monitored by means of thin-layer chromatography (TLC). IR spectra were measured on a FIR-360 spectrometer. <sup>1</sup>H NMR spectra were measured on a Bruker DRX500 NMR spectrometer using tetramethylsilane (TMS) as an internal standard and dimethylsulfoxide (DMSO-d<sub>6</sub>) as solvent. Elemental analyses were carried out using a Vario EL III analyzer. Reactions were carried out in a WF-4000 M microwave reaction system.

#### General Procedure for the Preparation of 3-Amino-1-aryl-8bromo-2,4-dicyano-9*H*-fluorenes (4)

A flask (50 ml) charged with arylaldehyde 1 (2 mmol), 4-bromo-indan-1-one 2 (2 mmol), malononitrile 3 (4.5 mmol), sodium hydroxide (5 mmol), and water (10 ml) was placed in microwave reaction system, connected with refluxing equipment. The mixture was irradiated for 6–7 min at 100 °C with the output of 400 W. After completion of the reaction (monitored by TLC), the mixture was kept at room temperature for several hours, filtered to give precipitation, and washed with ethanol.

The crystalline product was obtained from recrystallization with ethanol. All the products were characterized by FTIR and <sup>1</sup>H NMR.

#### 3-Amino-8-bromo-1-phenyl-2,4-dicyano-9H-fluorene (4a)

Yellow crystals; FTIR (KBr):  $\nu$  3449, 3343, 3237, 2210, 1636, 1559, 1467, 1367, 1305, 1287, 1121, 798, 759, 709, 696. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.63 (s, 2H, CH<sub>2</sub>), 6.81 (s, 2H, NH<sub>2</sub>), 7.50–7.58 (m, 6H, ArH), 7.73 (d, 1H, ArH), 8.35 (d, 1H, ArH). Anal. calcd. for C<sub>21</sub>H<sub>12</sub>BrN<sub>3</sub>: C, 65.30; H, 3.13; N, 10.88. Found: C, 65.48; H, 3.06; N, 10.81.

#### 3-Amino-8-bromo-1-(3-methylphenyl)-2,4-dicyano-9H-fluorene (4b)

Pale yellow crystals; FTIR (KBr):  $\nu$  3475, 3351, 3237, 2210, 1635, 1558, 1467, 1387, 1364, 1307, 1287, 1122, 796, 759, 724, 697. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  2.41 (s, 3H, CH<sub>3</sub>), 3.63 (s, 2H, CH<sub>2</sub>), 6.80 (s, 2H, NH<sub>2</sub>), 7.35–7.56 (m, 5H, ArH), 7.74 (d, 1H, ArH), 8.35 (d, 1H, ArH). Anal. calcd. for C<sub>22</sub>H<sub>14</sub>BrN<sub>3</sub>: C, 66.01; H, 3.53; N, 10.50. Found: C, 66.17; H, 3.60; N, 10.30.

#### 3-Amino-8-bromo-1-(Furan-2-yl)-2,4-dicyano-9H-fluorene (4c)

Yellow crystals; FTIR (KBr):  $\nu$  3444, 3348, 3238, 2208, 1639, 1561, 1547, 1480, 1423, 1384, 1359, 1307, 1126, 1029, 787, 756. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  4.00 (s, 2H, CH<sub>2</sub>), 6.78 (s, 2H, NH<sub>2</sub>), 7.38–7.77 (m, 4H, ArH), 8.11 (d, 1H, ArH), 8.33 (d, 1H, ArH). Anal. calcd. for C<sub>19</sub>H<sub>10</sub>BrN<sub>3</sub>O: C, 60.66; H, 2.68; N, 11.17. Found: C, 60.85; H, 2.62; N, 11.11.

#### 3-Amino-8-bromo-1-(Naphthalene-1-yl)-2,4-dicyano-9H-fluorene (4d)

Yellow crystals; IR (KBr):  $\nu$  3470, 3412, 3346, 3236, 3082, 2207, 1633, 1555, 1515, 1464, 1406, 1376, 1289, 1126, 792, 759, 708. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  4.02 (s, 2H, CH<sub>2</sub>), 6.93 (s, 2H, NH<sub>2</sub>), 7.48–7.74 (m, 6H, ArH), 7.94–8.14 (m, 3H, ArH), 8.39 (d, 1H, ArH). Anal. calcd. for C<sub>25</sub>H<sub>14</sub>BrN<sub>3</sub>: C, 68.82; H, 3.23; N, 9.63. Found: C, 67.00; H, 3.15; N, 9.51.

#### 3-Amino-8-bromo-1-(Thiophen-2-yl)-2,4-dicyano-9H-fluorene (4e)

Yellow crystals; FTIR (KBr):  $\nu$  3456, 3412, 3357, 3232, 2211, 1631, 1557, 1524, 1386, 1363, 1282, 1123, 1082, 803, 775, 759, 716. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.83 (s, 2H, CH<sub>2</sub>), 6.85 (s, 2H, NH<sub>2</sub>), 7.31 (t, 1H, ArH), 7.52–7.60 (m, 2H, ArH), 7.77 (d, 1H, ArH), 7.91 (d, 1H, ArH), 8.36 (d, 1H, ArH). Anal. calcd. for C<sub>19</sub>H<sub>10</sub>BrN<sub>3</sub>S: C, 58.17; H, 2.57; N, 10.71. Found: C, 58.08; H, 2.62; N, 10.75.

#### 3-Amino-8-bromo-1-(Pyridine-4-yl)-2,4-dicyano-9H-fluorene (4f)

Yellow crystals; FTIR (KBr): ν 3483, 3388, 3250, 2210, 1662, 1559, 1466, 1409, 1365, 1306, 1283, 1123, 1044, 830, 796, 7757, 693. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ

3.67 (s, 2H, CH<sub>2</sub>), 6.93 (s, 2H, NH<sub>2</sub>), 7.55 (t, 1H, ArH), 7.65 (d, 2H, ArH), 7.77 (d, 1H, ArH), 8.37 (d, 1H, ArH), 8.81 (d, 2H, ArH). Anal. calcd. for C<sub>20</sub>H<sub>11</sub>BrN<sub>4</sub>: C, 62.03; H, 2.86; N, 14.47. Found: C, 62.14; H, 2.80; N, 14.38.

#### 3-Amino-8-bromo-1-(3,4-difluorophenyl)-2,4-dicyano-9H-fluorene (4g)

Pale yellow crystals; FTIR (KBr):  $\nu$  3461, 3414, 3238, 2210, 1707, 1636, 1601, 1518, 1428, 1382, 1306, 1268, 1119, 983, 797, 771, 741. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.67 (s, 2H, CH<sub>2</sub>), 6.90 (s, 2H, NH<sub>2</sub>), 7.44–7.98 (m, 5H, ArH), 8.35 (d, 1H, ArH). Anal. calcd. for C<sub>21</sub>H<sub>10</sub>BrF<sub>2</sub>N<sub>3</sub>: C, 59.74; H, 2.39; N, 9.95. Found: C, 59.92; H, 2.32; N, 9.87.

#### 3-Amino-8-bromo-1-(3-fluorophenyl)-2,4-dicyano-9H-fluorene (4h)

Pale yellow crystals; FTIR (KBr):  $\nu$  3458, 3342, 3237, 2208, 1636, 1572, 1468, 1400, 1378, 1308, 1258, 1121, 876, 794, 761, 716, 688. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.66 (s, 2H, CH<sub>2</sub>), 6.90 (s, 2H, NH<sub>2</sub>), 7.38–7.45 (m, 2H, ArH), 7.54 (t, 2H, ArH), 7.60–7.68 (m, 1H, ArH), 7.76 (d, 1H, ArH), 8.35 (d, 1H, ArH). Anal. calcd. for C<sub>21</sub>H<sub>11</sub>BrFN<sub>3</sub>: C, 62.40; H, 2.74; N, 10.39. Found: C, 62.56; H, 2.69; N, 10.33.

#### X-Ray Structure Determination of 4a

Yellow block crystals,  $C_{21}H_{12}BrN_3$ , M = 386.25,  $0.20 \times 0.10 \times 0.10$  mm, monoclinic, space group P21/N, a = 10.437(2) Å, b = 7.2840(15) Å, c = 22.025(4) Å,  $\alpha = 90.00^{\circ}$ ,  $\beta = 90.45(3)^{\circ}$ ,  $\gamma = 90.00^{\circ}$ , V = 1674.4(6) Å<sup>3</sup>, Z = 4, Dc = 1.532 g cm<sup>-3</sup>. F(000) = 776,  $\mu$  (Mo K $\alpha$ ) = 2.463 mm<sup>-1</sup>. Intensity data were collected using a Nonius CAD4 diffract-ometer at 293(2) K, graphite monochromator Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), using w/2q scan mode with  $1.85^{\circ} < \theta < 25.26^{\circ}$ . A total of 3219 reflections were collected with 3043 unique ones ( $R_{int} = 0.0621$ ), of which 1603 reflections were observed with  $I > 2\sigma$  (I). The final R and wR values were 0.0660 and 0.1185, s = 1.009, ( $\Delta/\sigma$ )<sub>max</sub> = 0.000.

#### REFERENCES

- Young, D. D.; Torres-Kolbus, J.; Deiters, A. Microwave-assisted synthesis of unnatural amino acids. *Bioorg. Med. Chem. Lett.* 2008, 18, 5478–5480.
- Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. Microwave-assisted organic synthesis—A review. *Tetrahedron* 2001, *57*, 9225–9283.
- 3. Caddick, S. Microwave-assisted organic reactions. Tetrahedron 1995, 51, 10403-10432.
- Singh, A. K.; Shukla, S. K.; Ahamad, I.; Quraishi, M. A. Solvent-free microwave-assisted synthesis of 1H-indole-2,3-dione derivatives. J. Heterocycl. Chem. 2009, 46, 571–574.
- Shi, F.; Zhou, D.; Tu, S.; Shao, Q.; Li, C.; Cao, L. An efficient microwave-assisted synthesis of furo-3,4-b 4,7-phenanthroline and indeno-2,1-b4,7-phenanthroline derivatives in water. J. Heterocycl. Chem. 2008, 45, 1065–1070.
- Reddy, T. R. K.; Mutter, R.; Heal, W.; Guo, K.; Gillet, V. J.; Pratt, S.; Chen, B. Library design, synthesis, and screening: Pyridine dicarbonitriles as potential prion disease therapeutics. J. Med. Chem. 2006, 49, 607–615.

- Paul, S.; Gupta, R.; Loupy, A. Improved synthesis of 2-amino-3-cyanopyridines in solvent free conditions under microwave irradiation. J. Chem. Res., Sunop. 1998, 6, 330–331.
- Burkett, B. A.; Ting, S. Z.; Gan, G. C. S.; Chai, C. L. L. Microwave-assisted synthesis of azetidines in aqueous media. *Tetrahedron Lett.* 2009, 50, 6590–6592.
- Jia, R.; Tu, S.; Zhang, Y.; Jiang, B.; Zhang, Y.; Yao, C.; Shi, F. An efficient and greener approach to the synthesis of 3,5-dicyanopyridin-2 (1H)-one derivatives in aqueous media under microwave irradiation conditions. J. Heterocycl. Chem. 2007, 44, 1177–1180.
- Carpita, A.; Ribecai, A. Microwave-assisted synthesis of indole derivatives via cycloisomerization of 2-alkynylanilines in water without added catalysts, acids, or bases. *Tetrahedron Lett.* 2009, 50, 6877–6881.
- Cui, S.-L.; Lin, X.-F.; Wang, Y.-G.. Parallel synthesis of strongly fluorescent polysubstituted 2,6-dicyanoanilines via microwave-promoted multicomponent reaction. J. Org. Chem. 2005, 70, 2866–2869.
- Chen, X.; Zhao, Z.; Liu, Y.; Lu, P.; Wang, Y.-G. Synthesis and properties of 1-(4aminophenyl)-2,4-dicyano-3-diethylamino-9,9-diethylfluorenes: Potential fluorescent material. *Chem. Lett.* 2008, *37*, 570–571.
- Dumur, F.; Gautier, N.; Gallego-Planas, N.; Sahin, Y.; Levillain, E.; Mercier, N. Hudhomme, P. Novel fused D-A dyad and A-D-A triad incorporating tetrathiafulvalene and p-benzoquinone. J. Org. Chem. 2004, 69, 2164–2177.
- Chen, X.-H.; Zhao, Z.; Liu, Y.; Lu, P.; Wang, Y.-G. Synthesis and properties of 1-(4-aminophenyl)-2,4-dicyano-3-diethylamino-9,9-diethyl-fluorenes: Potential fluorescent material. *Chem. Lett.* 2008, *37*, 570–571.
- Ochi, T.; Yamaguchi, Y.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. Rod-shaped oligophenyleneethynylenes modified by donor and acceptor groups in a block manner: Synthesis and light-emitting characteristics. *Chem. Lett.* 2007, *36*, 794–795.
- Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. High-performance organic light-emitting diodes based on intramolecular charge-transfer emission from donor-acceptor molecules: Significance of electron-donor strength and molecular geometry. *Adv. Funct. Mater.* 2006, 16, 1057–1066.
- 17. Brown, A. R.; Pomp, A.; Hart, C. M.; de Leeuw, D. M. Logic gates made from polymer transistors and their use in ring oscillators. *Science* **1995**, *270*, 972–974.
- Ishihara, T.; Kakuta, H.; Moritani, H.; Ugawa, T.; Sakamoto, S.; Tsukamoto, S. I.; Yanagisawa, I. Syntheses and biological evaluation of novel quinuclidine derivatives as squalene synthase inhibitors. *Bioorg. Med. Chem.* 2003, *11*, 2403–2414.
- Weitzberg, M.; Burch, R. M. Pharmaceutical compositions and methods for treating inflammation. WO Patent 9015602, 1990.
- Wang, X.-S.; Zhang, M.-M.; Li, Q.; Yao, C.-S.; Tu, S.-J. An improved and clean procedure for the synthesis of one-donor poly-acceptors systems containing 2,6-dicyanoamine moiety in aqueous media catalyzed by TEBAC in the presence and absence of K<sub>2</sub>CO<sub>3</sub>. *Tetrahedron* 2007, 24, 5265–5273.
- Rong, L.; Han, H.; Jiang, H.; Tu, S. Efficient and facile synthesis of 3-amino-1-aryl-9H-fluorene-2,4-dicarbonitrile under solvent-free conditions. *Synth. Commun.* 2009, 39, 3493–3499.
- Wang, X.-S.; Zhang, M.-M.; Li, Q.; Yao, C.-S.; Tu, S.-J. An improved and clean procedure for the synthesis of one-donor poly-acceptors systems containing 2,6-dicyanoamine moiety in aqueous media catalyzed by TEBAC in the presence and absence of K<sub>2</sub>CO<sub>3</sub>. *Tetrahedron* 2007, *63*, 5265–5273.