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

# Malononitrile-Catalyzed and Highly Selective Method for the Synthesis of 2-((E)-1,3-Diarylallylidene)malononitriles in Ionic Liquid

Xiang-Shan Wang [a b], Mei-Mei Zhang [b], Qing Li [a] & Chang-Sheng Yao [a]

[a] School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou Jiangsu, China

[b] Key Laboratory of Biotechnology for Medical Plant, Xuzhou Normal University, Xuzhou Jiangsu, China

Published online: 03 Aug 2009.

To cite this article: Xiang-Shan Wang , Mei-Mei Zhang , Qing Li & Chang-Sheng Yao (2009) Malononitrile-Catalyzed and Highly Selective Method for the Synthesis of 2-((E)-1,3-Diarylallylidene)malononitriles in Ionic Liquid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:17, 3045-3059

To link to this article: http://dx.doi.org/10.1080/00397910902730903

*Synthetic Communications*®, 39: 3045–3059, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910902730903

Taylor & Francis
Taylor & Francis Group



# Malononitrile-Catalyzed and Highly Selective Method for the Synthesis of 2-((*E*)-1,3-Diarylallylidene)malononitriles in Ionic Liquid

**Xiang-Shan Wang,[1,2] Mei-Mei Zhang,[2] Qing Li,[1] and Chang-Sheng Yao[1]**

[1]School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou Jiangsu, China
[2]Key Laboratory of Biotechnology for Medical Plant, Xuzhou Normal University, Xuzhou Jiangsu, China

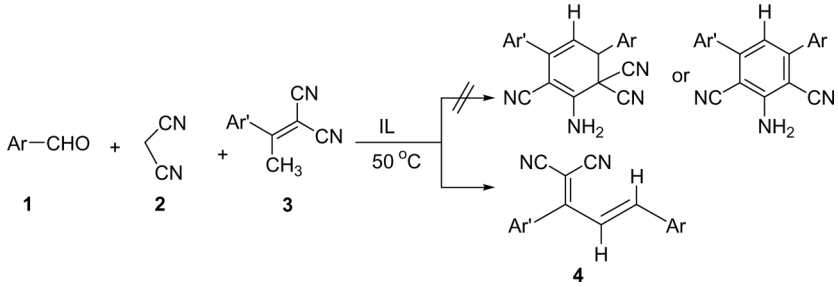
**Abstract:** The green and highly selective reactions of aromatic aldehydes, malononitrile, and 2-(1-arylethylidene)malononitriles in ionic liquid of [bmim$^+$]Br$^-$ at 50°C unexpectedly gave 2-((*E*)-1,3-diarylallylidene)malononitriles. The modification of the reaction used 10 mol% malononitrile as catalyst at 90°C in [bmim$^+$][$BF_4^-$]. A possible reaction mechanism for the formation of the product was proposed based on further experimental results. 2-((*E*)-1,3-Diarylallylidene) malononitriles were not detected at all in the designed reaction of aromatic aldehyde and 2-(1-arylethylidene)malononitriles at the same reaction conditions.

**Keywords:** 2-(1-Arylethylidene)malononitrile, 1,3-diarylallylidenemalononitrile, ionic liquid, malononitrile, synthesis

## INTRODUCTION

Ionic liquids are generally salts of quaternary ammonium species with poorly coordinating ions and liquids at temperature less than 100°C; they

Received October 1, 2008.
Address correspondence to Xiang-Shan Wang, School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou Jiangsu 221116, China. E-mail: xswang1974@yahoo.com




*Scheme 1.* Reaction of **1**, **3**, and **2** in ionic liquid of [bmim]Br.

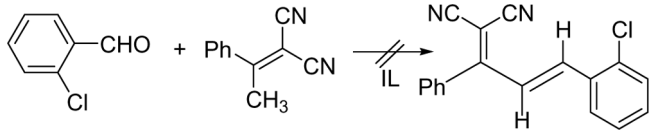


have attracted increasing interest in the context of green synthesis in recent times. Ionic liquids were initially introduced as alternative green reaction media because of their unique chemical and physical properties: nonvolatility, nonflammability, thermal stability, and controlled miscibility.[1,2] The possibility of recycling them and the low vapor frame also ensure their use in environmentally friendly technologies. They have recently attracted considerable interest as solvents for a large number of organic reactions because they are immiscible with many organic solvents.[3–9] As a part of our ongoing program to apply ionic liquids as green media in organic synthesis,[10,11] herein we report an improved reaction of aromatic aldehyde and 2-(1-arylethylidene)malononitrile in ionic liquid for the synthesis of 2-((*E*)-1,3-diarylallylidene)malononitriles catalyzed by malononitrile. This reaction has advantages of good yield, operational simplicity, and good selectivity.

We have previously reported an improved and green synthesis of 2-amino-4,6-diarylcyclohexa-2,4-diene-1,1,3-tricarbonitrile derivatives in water.[12] However, the desired 2,6-dicyanoaniline moieties were not detected in this triethylbenzylammonium chloride (TEBAC)/water system. To obtain these acceptor–donor–acceptor (A-D-A) systems in a multicomponent reaction, we performed a three-component reaction of aromatic aldehyde, malononitrile, and 2-(1-arylethylidene)malononitrile in ionic liquid of [bmim$^+$] Br$^-$ at 50°C. Unexpectedly, it gave the highly selective product of 2-((*E*)-1,3-diarylallylidene)malononitrile rather than 2,6-dicyanoaniline moiety or cyclohexa-2,4-diene-1,1,3-tricarbonitrile derivative (Scheme 1).

## RESULTS AND DISCUSSION

According to the structure of product, the malononitrile may attend to the reaction but lose at last, so we try to obtain the product **4** without




***Scheme 2.*** Reaction of **1a** and **3a** in ionic liquid without **2**.

malononitrile by a reaction of the 2-chlorobenzaldehyde and 1-phenylethylidenemalononitrile in ionic liquid at the same reaction conditions (Scheme 2), but it failed. It should be noted that the designed reaction could take place in ordinary organic solvent.[13–15] However, a base such as piperidine or triethylamine should be added; furthermore, the yields of the reported reactions were poor (69–80%).

An interesting conclusion could be made that the malononitrile in this reaction was a catalyst. Subsequently, the reaction of 2-chlorobenzaldehyde and 1-phenylethylidenemalononitrile was used as a model reaction to optimize the conditions. A summary of the optimization experiment is provided in Table 1. The results showed that no reaction

**Table 1.** Synthesis of **4a** in ionic liquid at different reaction conditions[a]

| Entry | Temp. (°C) | 2 (mol%) | Ionic liquid[b] | Time (h) | Yield[c] (%) |
|---|---|---|---|---|---|
| 1 | rt | 10 | [bmim$^+$][BF$_4^-$] | 6 | 0 |
| 2 | 50 | 10 | [bmim$^+$][BF$_4^-$] | 6 | 83 |
| 3 | 90 | 5 | [bmim$^+$][BF$_4^-$] | 6 | 78 |
| 4 | 90 | 10 | [bmim$^+$][BF$_4^-$] | 6 | 93 |
| 5 | 90 | 20 | [bmim$^+$][BF$_4^-$] | 6 | 86 |
| 6 | 90 | 10 | [bmim$^+$][BF$_4^-$] | 3 | 83 |
| 7 | 90 | 10 | [bmim$^+$][BF$_4^-$] | 9 | 92 |
| 8 | 90 | 10 | [emim$^+$]Br$^-$ | 6 | 82 |
| 9 | 90 | 10 | [pmim$^+$]Br$^-$ | 6 | 84 |
| 10 | 90 | 10 | [bmim$^+$]Br$^-$ | 6 | 86 |
| 11 | 90 | 10 | [emim$^+$][BF$_4^-$] | 6 | 89 |
| 12 | 90 | 10 | [pmim$^+$][BF$_4^-$] | 6 | 90 |
| 13 | 90 | Piperidine[d] | [bmim$^+$][BF$_4^-$] | 6 | 76 |
| 14 | 80 | Piperidine[13] | Ethanol | 3 | 80 |

[a]Reaction conditions: 1 mL ionic liquid, 2 mmol 2-chlorobenzaldehyde, and 2 mmol 1-phenylethylidenemalononitrile.

[b]bmim, 1-butyl-3-methylimidazolium; emim, 1-ethyl-3-methylimidazolium; pmim, 1-methyl-3-propylimidazolium.

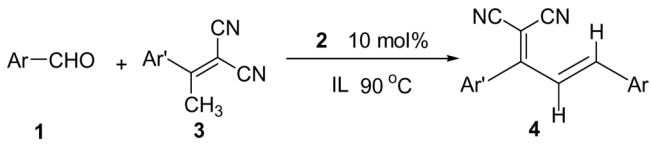
[c]Isolated yields.

[d]Reaction conditions: 1 mL ionic liquid, 2 mmol 2-chlorobenzaldehyde, 2 mmol 1-phenylethylidenemalononitrile, 10 mol% piperidine.

took place at room temperature (Table 1, entry 1). To our delight, the reaction proceeded smoothly at 90°C in good yield. Similar reactions were then carried out in the presence of 5%, 10%, and 20 mol% of malononitrile. The results from Table 1 (entries 3, 4, and 5) showed that 10 mol% malononitrile at 90°C in ionic liquid gave the best yield. Higher loading of the catalyst did not improve the yield to a great extent. To find the optimum reaction time, the reaction was carried out in ionic liquid of [bmim$^+$] [$BF_4^-$] for 3, 6, or 9 h (Table 1, entries 4, 6, and 7), leading to **4a** in 83%, 93%, and 92% yield, respectively. Thus, the optimal reaction temperature and reaction time are 90°C and 6 h, respectively. Using piperidine as basic catalyst only gave **4a** in 76% in ionic liquid media. Moreover, different ionic liquids were further investigated as shown in Table 1. We concluded that the [bmim$^+$] [$BF_4^-$] was the best ionic liquid for this reaction.

After the reaction was completed (monitored by thin-layer chromatography, TLC), the reaction mixture was cooled to room temperature, and then 5 mL water were added to the mixture. The solid was isolated by filtration. The water in the filtrate was removed by evaporation at reduced pressure, and the residue containing ionic liquid could be recovered easily at 80°C in vacuum after a few hours. The recovered ionic liquid could be reused for the same reaction. Alternatively, the ionic liquid was washed with ethyl acetate, followed by evaporation at 80°C in vacuum for a few hours, if it was used for other reactions with different substrates. Investigations using 2-chlorobenzaldehyde and 1-phenylethylidenemalononitrile as model substrates proved the successive reuse of the recovered ionic liquid. Even in the fourth cycle, the yield (92%) of product **4a** is fairly good.

To extend the reaction (Scheme 3) to a library system, various kinds of aromatic aldehydes **1** and 2-(1-arylethylidene)malononitriles **3** gave the corresponding 2-((*E*)-1,3-diarylallylidene) malononitriles **4**, and representative examples are shown in Table 2. All of **1** and **3** gave the desired products in good yields, either bearing electron-withdrawing groups (such as halide, nitro) or electron-donating groups (such as alkyl group, or alkoxyl group) under the same reaction conditions. However,




***Scheme 3.*** Reaction of **1** and **3** catalyzed by **2** in ionic liquid.

**Table 2.** Malononitrile-catalyzed reactions of aromatic aldehydes and 2-(1-arylethylidene)malononitriles in ionic liquid[a]

| Entry | Ar | Ar′ | Products | Time (h) | Yields (%)[b] |
|---|---|---|---|---|---|
| 1 | 2-$ClC_6H_4$ | $C_6H_5$ | **4a** | 6 | 93 |
| 2 | 2-$CH_3OC_6H_4$ | $C_6H_5$ | **4b** | 7 | 90 |
| 3 | 2-$NO_2C_6H_4$ | $C_6H_5$ | **4c** | 4 | 96 |
| 4 | 4-Cl-2-$NO_2C_6H_3$ | $C_6H_5$ | **4d** | 4 | 96 |
| 5 | 2,4-$Cl_2C_6H_3$ | $C_6H_5$ | **4e** | 5 | 92 |
| 6 | 3-$NO_2C_6H_4$ | $C_6H_5$ | **4f** | 6 | 90 |
| 7 | 3,4-$Cl_2C_6H_3$ | $C_6H_5$ | **4g** | 7 | 94 |
| 8 | 2-$ClC_6H_4$ | 4-$BrC_6H_4$ | **4h** | 5 | 96 |
| 9 | 2,4-$Cl_2C_6H_3$ | 4-$BrC_6H_4$ | **4i** | 5 | 92 |
| 10 | 2-$NO_2C_6H_4$ | 4-$BrC_6H_4$ | **4j** | 3 | 98 |
| 11 | 2-$ClC_6H_4$ | 4-$ClC_6H_4$ | **4k** | 5 | 90 |
| 12 | 2,4-$Cl_2C_6H_3$ | 4-$CH_3C_6H_4$ | **4l** | 4 | 92 |
| 13 | 3,4-$(CH_3)_2C_6H_3$ | 4-$CH_3OC_6H_4$ | **4m** | 8 | 88 |
| 14 | 2,4-$Cl_2C_6H_3$ | 4-$CH_3OC_6H_4$ | **4n** | 8 | 87 |
| 15 | 2-$ClC_6H_4$ | 4-$CH_3OC_6H_4$ | **4o** | 7 | 92 |
| 16 | 2-$NO_2C_6H_4$ | 4-$CH_3OC_6H_4$ | **4p** | 5 | 95 |
| 17 | 3,4-$Cl_2C_6H_3$ | 4-$CH_3OC_6H_4$ | **4q** | 7 | 92 |
| 18 | 3,4-$(CH_3O)_2C_6H_3$ | 2,4-$(CH_3)_2C_6H_3$ | **4r** | 8 | 89 |
| 19 | 2-$ClC_6H_4$ | 2,4-$(CH_3)_2C_6H_3$ | **4s** | 7 | 90 |
| 20 | 2-$ClC_6H_4$ | 3-$ClC_6H_4$ | **4t** | 5 | 90 |
| 21 | 2-$ClC_6H_4$ | 4-$FC_6H_4$ | **4u** | 5 | 95 |

[a]Reaction conditions: 1 mL ionic liquid, 2 mmol aromatic aldehyde **1**, 0.2 mmol malononitrile **2**, and 2 mmol 2-(1-arylethylidene)malononitrile **3**, 90°C.
[b]Isolated yields.



we failed to give the corresponding products, using *n*-butyraldehyde, *n*-heptaldehyde, and 3-indolealdehyde as reactants.

The structure of product **4h** was further confirmed by x-ray diffraction analysis, and the crystal structure of **4h** is shown in Fig. 1.

Although the detailed mechanism of the reaction has not been clarified yet, the formation of **4** can be tentatively explained by the pathway presented in Scheme 4. A sequential reaction of the Knoevenagel condensation and Michael addition reaction may take place, followed by losing a molecule of **2** to give the final product **4**.

To verify the mechanism, we performed each separate step of the reaction. The Knoevenagel condensation product, 2-chlorophenylidenemalononitrile **5,** was obtained in 92% yield; subsequently, product **5** was treated with 1-phenylethylidene malononitrile **3a** in ionic liquid (Scheme 5). As expected, intermediate product **5** reacted with **3a** to smoothly give the

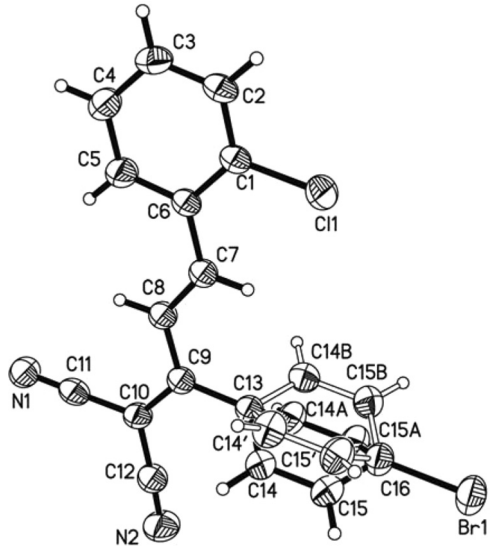
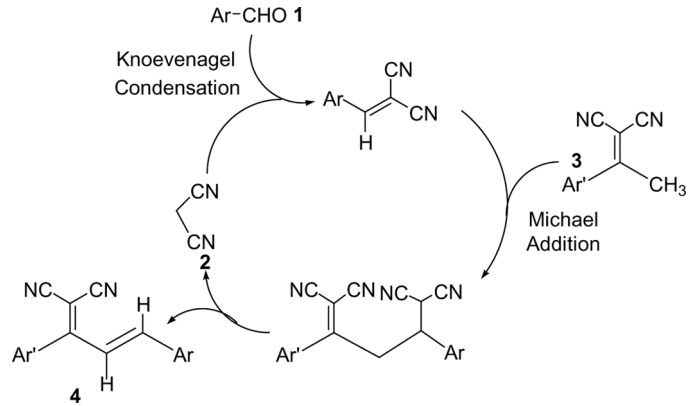
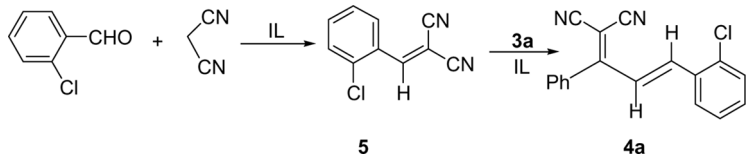


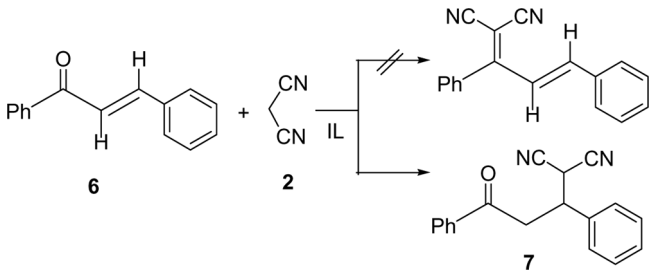

***Figure 1.*** Crystal structure of product **4h** with positional disorder in 4-bromobenzene ring.




***Scheme 4.*** Possible mechanism for the formation of products **4**.




***Scheme 5.*** Separate reactions of **1a**, **2**, and **3a** in ionic liquid.




*Scheme 6.* Reaction of chalcone **6** with malonitrile in ionic liquid.



corresponding **4a**. This result suggested that a Knoevenagel condensation took place during the reaction.

Furthermore, treating chalcone **6** with malononitrile for 12 h in ionic liquid at 90°C (Scheme 6) gave the Michael addition product **7** in 82% yield rather than the desired product **4**, which was in accordance to that of the reference reported.[16,17]

## EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. Infrared (IR) spectra were recorded on a Tensor 27 spectrometer in KBr pellets. $^1$H NMR spectra were obtained from solution in dimethy sulfoxide (DMSO)-$d_6$ with $Me_4Si$ as internal standard using an Inova-400 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 II analyzer.

### General Procedure for the Syntheses of 2-((*E*)-1,3-Diarylallylidene) malononitriles 4

A dry 50-mL flask was charged with aromatic aldehyde (2.0 mmol), malononitrile (0.013 g, 0.2 mmol), 2-(1-arylethylidene)malononitrile (2.0 mmol), and ionic liquid of [bmim$^+$][$BF_4^-$] (1 mL). The reaction mixture was stirred at 90°C for 3–8 h, and then 5 mL water were added to the mixture. The solid was isolated by filtration. The water in the filtrate was removed by evaporation at reduced pressure, and the ionic liquid could be recovered easily at 80°C in vacuum after a few hours. The crude yellow products were washed with water and purified by recrystallization from dimethyformanide (DMF) and water to give **4**.

## Data

2-((*E*)-3-(2-Chlorophenyl)-1-phenylallylidene)malononitrile **4a**

Pale yellow crystals; mp 151–153°C. IR (KBr): 3059, 2223, 1606, 1587, 1561, 1527, 1487, 1470, 1445, 1339, 1280, 1182, 1101, 1079, 1041, 967, 768, 734, 719, 703, 683 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.18 (d, $J = 15.6$ Hz, 1H, CH =), 7.47–7.50 (m, 5H, ArH +CH =), 7.60–7.66 (m, 4H, ArH), 8.00–8.02 (m, 1H, ArH). $^{13}C$ NMR (DMSO-$d_6$) δ: 84.1, 113.1, 114.0, 125.6, 127.3, 128.6, 129.0, 130.7, 131.7, 132.2, 132.46, 132.54, 133.3, 134.9, 143.6, 169.5. MS (m/z): 290 ($M^+$, 42), 255 (100), 227 (25), 178 (17). Anal. Calcd. for $C_{18}H_{11}ClN_2$: C, 74.36; H, 3.81; N, 9.64. Found: C, 74.52; H, 3.70; N, 9.68.

2-((*E*)-3-(2-Methoxylphenyl)-1-phenylallylidene)malononitrile **4b**

Pale yellow crystals; mp 136–138°C. IR (KBr): 3015, 2968, 2940, 2840, 2221, 1600, 1530, 1480, 1438, 1329, 1309, 1255, 1180, 1160, 1116, 1048, 1029, 978, 871, 763, 714, 701 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 3.78 (s, 3H, $CH_3O$), 7.01–7.05 (m, 1H, ArH), 7.08–7.11 (m, 2H, ArH), 7.45–7.49 (m, 3H, ArH +CH =), 7.58–7.65 (m, 4H, ArH), 7.72 (d, $J = 15.6$ Hz, 1H, CH =). Anal. Calcd. for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.57; H, 5.10; N, 9.90.

2-((*E*)-3-(2-Nitrophenyl)-1-phenylallylidene)malononitrile **4c**

Pale yellow crystals; mp 149–150°C. IR (KBr): 3067, 2223, 1607, 1569, 1524, 1487, 1441, 1352, 1321, 1299, 1214, 1165, 1102, 972, 855, 773, 749, 723, 699 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.30 (d, $J = 15.6$ Hz, 1H, CH =), 7.45 (d, $J = 15.6$ Hz, 1H, CH =), 7.55–7.73 (m, 6H, ArH), 7.84–7.87 (m, 1H, ArH), 7.99 (d, $J = 8.0$ Hz, 1H, ArH), 8.08 (d, $J = 8.4$ Hz, 1H, ArH). Anal. Calcd. for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95. Found: C, 71.72; H, 3.78; N, 13.79.

2-((*E*)-3-(4-Chloro-2-Nitrophenyl)-1-phenylallylidene)malononitrile **4d**

Pale yellow crystals; mp 179–181°C. IR (KBr): 3108, 3081, 2229, 1598, 1561, 1521, 1468, 1445, 1335, 1264, 1205, 1095, 1027, 972, 927, 877, 848, 777, 759, 737, 708 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.24 (d, $J = 15.6$ Hz, 1H, CH =), 7.51 (d, $J = 15.6$ Hz, 1H, CH =), 7.54–7.65 (m, 5H, ArH), 7.75 (dd, $J = 8.4$ Hz, $J' = 2.0$ Hz, 1H, ArH), 8.10–8.12

(m, 2H, ArH). Anal. Calcd. for $C_{18}H_{10}ClN_3O_2$: C, 64.39; H, 3.00; N, 12.52. Found: C, 64.51; H, 3.11; N, 12.55.

2-((*E*)-3-(2,4-Dichlorophenyl)-1-phenylallylidene)malononitrile **4e**

Pale yellow crystals; mp 129–130°C. IR (KBr): 3060, 2223, 1604, 1581, 1531, 1488, 1469, 1442, 1389, 1325, 1305, 1280, 1214, 1143, 1100, 1049, 972, 887, 844, 817, 756, 699 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.10 (d, $J = 15.6$ Hz, 1H, CH =), 7.53–7.66 (m, 7H, ArH +CH =), 7.73 (d, $J = 2.0$ Hz, 1H, ArH), 8.08 (d, $J = 8.8$ Hz, 1H, ArH). Anal. calcd. for $C_{18}H_{10}Cl_2N_2$: C, 66.48; H, 3.10; N, 8.61. Found: C, 66.35; H, 3.17; N, 8.55.

2-((*E*)-3-(3-Nitrophenyl)-1-phenylallylidene)malononitrile **4f**

Pale yellow crystals; mp 169–171°C. IR (KBr): 3087, 2227, 1607, 1547, 1530, 1478, 1354, 1099, 985, 812, 777, 738, 702 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.12 (d, $J = 16.0$ Hz, 1H, CH =), 7.54–7.76 (m, 7H, ArH +CH =), 8.22 (d, $J = 7.6$ Hz, 1H, ArH), 8.28 (dd, $J = 8.0$ Hz, $J' = 2.0$ Hz, 1H, ArH), 8.57 (s, 1H, ArH). Anal. calcd. for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95. Found: C, 71.88; H, 3.59; N, 13.79.

2-((*E*)-3-(3,4-Dichlorophenyl)-1-phenylallylidene)malononitrile **4g**

Pale yellow crystals, mp 190–192°C. IR (KBr): 3058, 3027, 2228, 1609, 1585, 1547, 1529, 1488, 1472, 1443, 1394, 1343, 1317, 1272, 1215, 1135, 1105, 1074, 1029, 982, 810, 779, 748, 699 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 6.92 (d, $J = 15.2$ Hz, 1H, CH =), 7.51–7.53 (m, 2H, ArH), 7.61–7.76 (m, 6H, ArH + CH =), 8.08 (d, $J = 2.0$ Hz, 1H, Ar−H). Anal. calcd. for $C_{18}H_{10}Cl_2N_2$: C, 66.48; H, 3.10; N, 8.61. Found: C, 66.44; H, 3.22; N, 8.45.

2-((*E*)-1-(4-Bromophenyl)-3-(2-chlorophenyl)allylidene) malononitrile **4h**

Pale yellow crystals, mp 180–184°C. IR (KBr): 3061, 2221, 1602, 1561, 1532, 1485, 1469, 1444, 1391, 1338, 1323, 1286, 1098, 1071, 1039, 1011, 966, 824, 766, 750 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.16 (d, $J = 15.6$ Hz, 1H, CH =), 7.47–7.55 (m, 5H, ArH), 7.58 (d, $J = 15.6$ Hz, 1H, CH =), 7.85 (d, $J = 8.4$ Hz, 2H, ArH), 8.01–8.03 (m, 1H, ArH). $^{13}C$ NMR (DMSO-$d_6$) δ: 83.7, 113.3, 114.1, 127.5, 128.6, 128.9, 129.4, 129.5, 130.7, 131.9, 132.3, 133.3, 134.8, 143.6, 170.8. MS (m/z): 370 ($M^+$, 10),

289 (100), 254 (25), 227 (20). Anal. calcd. for $C_{18}H_{10}BrClN_2$: C, 58.49; H, 2.73; N, 7.58. Found: C, 58.62; H, 2.70; N, 7.54.

Crystal Data for **4h**

$C_{36}H_{20}Br_2Cl_2N_4$; $M = 739.28$, pale yellow block crystals, $0.28 \times 0.26 \times 0.12$ mm, orthorhombic, space group P nma, $a = 20.900(4)$, $b = 7.0710(11)$, $c = 10.9170$ (18) Å, $\alpha = \beta = \gamma = 90$ °, $V = 1613.4(5)$ Å$^3$, $Z = 2$, $Dc = 1.522$ g·cm$^{-3}$. $F(000) = 736$, μ (MoKα) $= 2.710$ mm$^{-1}$. Intensity data were collected on a CCD area detector with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) using phi and omega scans mode with $2.10° < \theta < 26.26°$. A total of 1782 unique reflections were measured, and 1058 reflections with $I > 2\sigma(I)$ were used in the refinement. Structure solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to $R = 0.0494$ and $wR = 0.1146$.

2-((*E*)-1-(4-Bromophenyl)-3-(2,4-dichlorophenyl)allylidene)malononitrile **4i**

Pale yellow crystals; mp 170–172°C. IR (KBr): 3072, 2224, 1607, 1578, 1527, 1485, 1468, 1388, 1336, 1317, 1213, 1187, 1148, 1103, 1069, 1050, 976, 911, 827, 777, 729 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ: 7.08 (d, $J = 15.6$ Hz, 1H, CH=), 7.51–7.60 (m, 4H, ArH +CH=), 7.72 (d, $J = 2.0$ Hz, 1H, ArH), 7.85 (d, $J = 8.4$ Hz, 2H, ArH), 8.06 (d, $J = 8.4$ Hz, 1H, ArH). Anal. calcd. for $C_{18}H_9BrCl_2N_2$: C, 53.50; H, 2.24; N, 6.93. Found: C, 53.51; H, 2.17; N, 6.78.

2-((*E*)-1-(4-Bromophenyl)-3-(2-nitrophenyl)allylidene)malononitrile **4j**

Pale yellow crystals; mp 170–172°C. IR (KBr): 3061, 2222, 1607, 1586, 1569, 1519, 1486, 1441, 1395, 1348, 1269, 1211, 1100, 1074, 1011, 968, 855, 829, 789, 745, 700 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ: 7.32 (d, $J = 15.6$ Hz, 1H, CH), 7.42 (d, $J = 15.6$ Hz, 1H, CH), 7.53 (d, $J = 7.2$ Hz, 2H, ArH), 7.69–7.73 (m, 1H, ArH), 7.82–7.88 (m, 3H, ArH), 7.98 (d, $J = 7.6$ Hz, 1H, ArH), 8.10 (d, $J = 8.0$ Hz, 1H, ArH). Anal. calcd. for $C_{18}H_{10}BrN_3O_2$: C, 56.86; H, 2.65; N, 11.05; Found: C, 56.80; H, 2.66; N, 10.94.

2-((*E*)-1-(4-Chlorophenyl)-3-(2-chlorophenyl)allylidene)malononitrile **4k**

Pale yellow crystals; mp 163–165°C. IR (KBr): 3062, 2220, 1604, 1565, 1532, 1469, 1337, 1317, 1288, 1091, 1040, 1013, 828, 769, 756 cm$^{-1}$. $^1$H

NMR (DMSO-$d_6$) δ: 7.17 (d, $J = 15.6$ Hz, 1H, CH), 7.48–7.56 (m, 3H, ArH), 7.59 (d, $J = 15.6$ Hz, 1H, CH), 7.61 (d, $J = 8.4$ Hz, 2H, ArH), 7.72 (d, $J = 8.4$ Hz, 2H, ArH), 8.02–8.04 (m, 1H, ArH). Anal. calcd. for $C_{18}H_{10}Cl_2N_2$: C, 66.48; H, 3.10; N, 8.61. Found: C, 66.30; H, 3.19; N, 8.65.

2-((*E*)-3-(2,4-Dichlorophenyl)-1-(4-methylphenyl)allylidene) malononitrile **4l**

Pale yellow crystals; mp 128–130°C. IR (KBr): 3066, 3031, 2222, 1606, 1584, 1547, 1517, 1499, 1471, 1387, 1342, 1303, 1210, 1187, 1146, 1109, 1047, 989, 949, 858, 820, 761, 726 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.13 (d, $J = 15.6$ Hz, 1H, CH), 7.41–7.45 (m, 4H, ArH), 7.55–7.58 (m, 2H, ArH +CH), 7.71 (s, 1H, ArH), 8.04 (d, $J = 8.8$ Hz, 1H, ArH). Anal. calcd. for $C_{19}H_{12}Cl_2N_2$: C, 67.27; H, 3.57; N, 8.26. Found: C, 67.11; H, 3.69; N, 8.29.

2-((*E*)-3-(3,4-Dimethylphenyl)-1-(4-methoxylphenyl)allylidene) malononitrile **4m**

Pale yellow crystals; mp 127–128°C. IR (KBr): 3015, 2968, 2943, 2218, 1604, 1593, 1524, 1493, 1460, 1442, 1416, 1382, 1342, 1298, 1237, 1205, 1176, 1103, 1021, 965, 845, 818 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 2.24 (s, 3H, $CH_3$), 2.26 (s, 3H, $CH_3$), 3.87 (s, 3H, $CH_3O$), 6.93 (d, $J = 15.6$ Hz, 1H, CH), 7.15–7.17 (m, 2H, ArH), 7.23–7.25 (m, 1H, ArH), 7.43–7.51 (m, 5H, ArH +CH). Anal. calcd. for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.35; H, 5.70; N, 8.93.

2-((*E*)-3-(2,4-Dichlorophenyl)-1-(4-methoxylphenyl)allylidene) malononitrile **4n**

Pale yellow crystals; mp 187–188°C. IR (KBr): 3052, 2221, 1604, 1583, 1497, 1471, 1346, 1309, 1267, 1181, 1103, 1024, 995, 948, 874, 836, 812 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 3.87 (s, 3H, $CH_3O$), 7.16–7.21 (m, 3H, ArH +CH), 7.54–7.60 (m, 4H, ArH +CH), 7.75 (d, $J = 2.0$ Hz, 1H, ArH), 8.06 (d, $J = 8.8$ Hz, 1H, ArH). Anal. calcd. for $C_{19}H_{12}Cl_2N_2O$: C, 64.24; H, 3.41; N, 7.89. Found: C, 64.20; H, 3.53; N, 7.80.

2-((*E*)-3-(2-Chlorophenyl)-1-(4-methoxylphenyl)allylidene)malononitrile **4o**

Pale yellow crystals; mp 110–112°C. IR (KBr): 3009, 2222, 1602, 1574, 1521, 1504, 1470, 1442, 1342, 1312, 1265, 1186, 1031, 1000, 953, 841,

755 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 3.87 (s, 3H, $CH_3O$), 7.17 (d, $J = 8.8$ Hz, 2H, ArH), 7.26(d, $J = 15.6$ Hz, 1H, CH), 7.48–7.51 (m, 2H, ArH), 7.54–7.59 (m, 4H, ArH +CH), 8.01–8.03 (m, 1H, ArH). Anal. calcd. for $C_{19}H_{13}ClN_2O$: C, 71.14; H, 4.08; N, 8.73. Found: C, 71.03; H, 4.18; N, 8.80.

2-((*E*)-1-(4-Methoxylphenyl)-3-(2-nitrophenyl)allylidene)malononitrile **4p**

Pale yellow crystals; mp 188–190°C. IR (KBr): 3084, 3004, 2972, 2839, 2223, 1602, 1569, 1518, 1439, 1420, 1345, 1292, 1254, 1210, 1177, 1103, 1025, 983, 857, 838, 794, 749, 704 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 3.87 (s, 3H, $CH_3O$), 7.16 (d, $J = 8.4$ Hz, 2H, ArH), 7.36 (d, $J = 15.6$ Hz, 1H, CH), 7.42 (d, $J = 15.6$ Hz, 1H, CH), 7.57 (d, J = 8.4 Hz, 2H, ArH), 7.70–7.71 (m, 1H, ArH), 7.85–7.89 (m, 1H, ArH), 7.98 (d, $J = 8.0$ Hz, 1H, ArH), 8.10 (d, $J = 8.0$ Hz, 1H, ArH). Anal. calcd. for $C_{19}H_{13}N_3O_3$: C, 68.88; H, 3.95; N, 12.68. Found: C, 69.01; H, 3.87; N, 12.57.

2-((*E*)-3-(3,4-Dichlorophenyl)-1-(4-methoxylphenyl)allylidene) malononitrile **4q**

Pale yellow crystals; mp 161–163°C. IR (KBr): 3029, 2966, 2842, 2223, 1606, 1573, 1550, 1526, 1505, 1471, 1386, 1343, 1317, 1294, 1255, 1213, 1179, 1135, 1105, 1030, 981, 924, 836, 815, 727, 675 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 3.87 (s, 3H, $CH_3O$), 6.99 (d, $J = 15.6$ Hz, 1H, CH), 7.15 (d, $J = 8.4$ Hz, 2H, ArH), 7.51 (d, $J = 8.4$ Hz, 2H, ArH), 7.59 (d, $J = 15.6$ Hz, 1H, CH), 7.68–7.75 (m, 2H, ArH), 8.06 (s, 1H, ArH). Anal. calcd. for $C_{19}H_{12}Cl_2N_2O$: C, 64.24; H, 3.41; N, 7.89. Found: C, 64.38; H, 3.43; N, 7.82.

2-((*E*)-3-(3,4-Dimethoxylphenyl)-1-(2,4-dimethylphenyl)allylidene) malononitrile **4r**

Pale yellow crystals; mp 138–140°C. IR (KBr): 3002, 2966, 2933, 2837, 2218, 1611, 1591, 1574, 1518, 1461, 1439, 1418, 1342, 1302, 1284, 1241, 1171, 1140, 1024, 970, 858, 820, 799, 773 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 2.15 (s, 3H, $CH_3$), 2.38 (s, 3H, $CH_3$), 3.79 (s, 3H, $CH_3O$), 3.82 (s, 3H, $CH_3O$), 6.71 (d, $J = 15.2$ Hz, 1H, CH), 7.02 (d, $J = 8.8$ Hz, 1H, ArH), 7.14 (d, $J = 8.0$ Hz, 1H, ArH), 7.20 (d, $J = 7.6$ Hz, 1H, ArH), 7.25–7.30 (m, 3H, ArH), 7.46 (d, $J = 15.2$ Hz, 1H, CH). Anal. calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.60; H, 5.77; N, 8.25.

2-((*E*)-3-(2-Chlorophenyl)-1-(2,4-dimethylphenyl)allylidene) malononitrile **4s**

Pale yellow crystals; mp 158–160°C. IR (KBr): 3062, 2225, 1604, 1561, 1534, 1495, 1462, 1437, 1338, 1310, 1284, 1237, 1210, 1160, 1083, 1039, 963, 815, 763, 741, 726, 706 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 2.17 (s, 3H, $CH_3$), 2.37 (s, 3H, $CH_3$), 7.02 (d, $J = 15.6$ Hz, 1H, CH), 7.04–7.23 (m, 2H, ArH), 7.27 (s, 1H, ArH), 7.47–7.54 (m, 3H, ArH), 7.59 (d, $J = 15.6$ Hz, 1H, CH), 8.02–8.04 (m, 1H, ArH). Anal. calcd. for $C_{20}H_{15}ClN_2$: C, 75.35; H, 4.74; N, 8.79. Found: C, 75.30; H, 4.91; N, 8.97.

2-((*E*)-1-(3-ssssChlorophenyl)-3-(2-chlorophenyl)allylidene) malononitrile **4t**

Pale yellow crystals; mp 141–143°C. IR (KBr): 3064, 2226, 1602, 1562, 1526, 1466, 1436, 1409, 1333, 1312, 1283, 1194, 1112, 1079, 1051, 1037, 888, 849, 794, 775, 722, 704, 695 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.17 (d, $J = 15.6$ Hz, 1H, CH), 7.49–7.57 (m, 4H, ArH), 7.59 (d, $J = 15.6$ Hz, 1H, CH), 7.65–7.75 (m, 3H, ArH), 8.04–8.05 (m, 1H, ArH). Anal. calcd. for $C_{18}H_{10}Cl_2N_2$: C, 66.48; H, 3.10; N, 8.61. Found: C, 66.49; H, 3.20; N, 8.49.

2-((*E*)-3-(2-Chlorophenyl)-1-(4-fluorophenyl)allylidene) malononitrile **4u**

Pale yellow crystals; mp 136–138°C. IR (KBr): 3051, 2223, 1603, 1562, 1532, 1466, 1340, 1285, 1238, 1210, 1159, 1094, 1043, 974, 838, 804, 763 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ: 7.17 (d, $J = 15.6$ Hz, 1H, CH), 7.47–7.54 (m, 5H, ArH), 7.59 (d, $J = 15.6$ Hz, 1H, CH), 7.64–7.67 (m, 2H, ArH), 8.01–8.04 (m, 1H, ArH). Anal. calcd. for $C_{18}H_{10}ClFN_2$: C, 70.02; H, 3.26; N, 9.07. Found: C, 69.90; H, 3.37; N, 9.00.

## CONCLUSION

In conclusion, we have discovered a green and highly selective method for the syntheses of 2-((*E*)-1,3-diarylallylidene)malononitriles by the reaction of aromatic aldehyde and 2-(1-arylethylidene)malononitrile in ionic liquid using 10 mol% malononitrile as catalyst. The noteworthy features of this procedure are mild reaction conditions, good yield, operational

simplicity, and an environmentally friendly procedure. Meanwhile, [bmim$^+$] [$BF_4^-$] could be reused for several rounds without significant loss of activity.

## ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (20802061), the Natural Science Foundation (08KJD150019), and Qing Lan Project (08QLT001) of Jiangsu Education Committee for financial support.



## REFERENCES

1. Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2084.
2. Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.* **2002**, *102*, 3667–3692.
3. Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. The Heck reaction in ionic liquids: A multiphasic catalyst system. *Org. Lett.* **1999**, *1*, 997–1000.
4. Shen, Z. L.; Ji, S. J.; Loh, T. P. Ionic liquid [omim][$PF_6$] as an efficient and recyclable reaction media for the cyanosilylation of aldehydes without Lewis acid or any special activation. *Tetrahedron Lett.* **2005**, *46*, 3137–3139.
5. Ren, R. X.; Wu, J. X. Mild conversion of alcohols to alkyl halides using halide-based ionic liquids at room temperature. *Org. Lett.* **2001**, *3*, 3727–3728.
6. Chen, S. L.; Ji, S. J.; Loh, T. P. Mukaiyama aldol reaction using ketene silyl acetals with carbonyl compounds in ionic liquids. *Tetrahedron Lett.* **2004**, *45*, 375–377.
7. Tao, X. L.; Lei, M.; Wang, Y. G. Ionic liquid supported synthesis of β-lactam library in ionic liquid batch. *Tetrahedron Lett.* **2007**, *48*, 5143–5146.
8. Ji, S.-J.; Zhou, M.-F.; Gu, D.-G.; Wang, S.-Y.; Loh, T.-P. Efficient synthesis of pis(indolyl)methanes catalyzed by Lewis acids in ionic liquids. *Synlett.* **2003**, (13), 2077–2080.
9. Yang, D.-H.; Chen, Z.-C.; Chen, S.-Y.; Zheng, Q.-G. Organic reactions in ionic liquids: ionic Liquid–accelerated three-component reaction: A rapid one-pot synthesis of 3-alkyl-5-[(*Z*)-arylmethylidene]-1,3-thiazolidine-2, 4-diones. *Synthesis* **2003**, (12), 1891–1895.
10. Wang, X. S.; Zhang, M. M.; Jiang, H.; Shi, D. Q.; Tu, S. J.; Wei, X. Y.; Zong, Z. M. An improved and benign synthesis of 9,10-diarylacridine-1,8-dione and indenoquinoline derivatives from 3-anilino-5,5-dimethylcyclohex-2-enones, benzaldehydes, and 1,3-dicarbonyl compounds in an ionic liquid medium. *Synthesis* **2006**, 4187–4199.
11. Wang, X. S.; Zhang, M. M.; Jiang, H.; Yao, C. S.; Tu, S. J. Three-component green synthesis of N-arylquinoline derivatives in ionic liquid [Bmim$^+$][$BF_4^-$]:

Reactions of arylaldehyde, 3-arylamino-5,5-dimethylcyclohex-2-enone, and active methylene compounds. *Tetrahedron* **2007**, *63*, 4439–4449.
12. Wang, X. S.; Zhang, M. M.; Jiang, H.; Yao, C. S.; Tu, S. J. An improved and clean procedure for the synthesis of one-donor polyacceptors systems containing 2,6-dicyanoamine moiety in aqueous media catalyzed by TEBAC in the presence and absence of $K_2CO_3$. *Tetrahedron* **2007**, *63*, 5265–5273.
13. Galil, F. M. A.; Elnagdi, M. H. α,β-Unsaturated nitriles in organic synthesis: A novel synthesis of biaryls and azabiaryls. *Liebigs Ann. Chem.* **1987**, 477–480.
14. El-Taweel, F. M. Nitriles in organic synthesis: Synthesis of aromatic amines, aminopyridines, pyrido[2,3-b]pyridine and pyrido[2,3-*d*]pyrimidine derivatives. *J. Prakt. Chem.* **1990**, *332*, 762–766.
15. Shestopalov, A. M.; Litvinov, V. P.; Sharanin, Y. A.; Khoroshilov, G. E. Regio- and stereoselectivity of reactions of azinium ylides with 1,3-butadienes. *Dokl. Akad. Nauk SSSR Ser. Khim.* **1990**, *312*, 1156–1160.
16. Tu, S. J.; Shi, D. Q.; Zhou, L. H.; Dai, G. Y. Michael addition reaction talyzed by potassium fluoride/alumina. *Huaxue Shiji* **1999**, *21*, 121–123, *Chem. Abstr.* **1999**, *130*, 311591.
17. Yao, C. S.; Gao, C. M.; Liu, H. Y.; Yu, C. X. The Michael reaction of chalcone and malononitrile without catalyst. *J. Xuzhou Normal Univ. (Nat. Sci. Ed.)* **2005**, *23*, 51–52, *Chem. Abstr.* **2006**, *144*, 323778.