

# Mesoporous KIT-6 Supported Ionic Liquids as New and Highly Effective Heterogeneous Catalysts for Three-component Synthesis of 2-Amino-3-cyano-4H-pyrans

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**Abstract:** A series of mesoporous KIT-6 supported ionic liquids were prepared and tested as effective and practical catalysts for the synthesis of 2-amino-3-cyano-4H-pyrans. The effects of type of catalysts, catalyst amount, and catalyst stability have also been investigated in detail, the catalyst KIT-6@ILMoO<sub>4</sub> exhibited excellent activity in good to excellent yields of 88 % – 98 %, may be attributed to the synergetic effect between hydroxyl groups of support beta and molybdate from the ionic liquid. In addition, the supported catalyst can be easily recovered and reused for six times still with satisfactory catalytic activity. Furthermore, a general synergetic catalytic mechanism for the reaction was proposed. Maybe this work employing KIT-6@ILMoO<sub>4</sub> as highly efficient and stable catalyst for the synthesis of 2-amino-3-cyano-4H-pyrans has potential commercial applications.

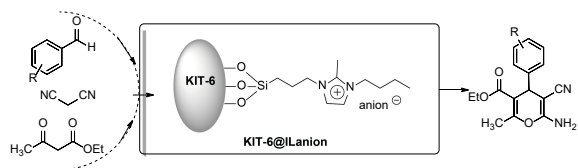
**Keywords:** 2-amino-3-cyano-4H-pyrans, heterogeneous catalysis, mesoporous beta zeolite, recyclable catalyst, supported ionic liquid.

## INTRODUCTION

**4H**-PYRANS, in particular 2-amino-3-cyano-4H-pyrans have attracted considerable attention as they are found to act as building blocks for the synthesis of many important drugs, herbicides, anticancer, and fine chemicals.<sup>[1,2]</sup> Thus, the synthesis of these compounds has revived the interests of synthetic organic chemists. Among the known methods, the most straightforward synthesis of these compounds involves the condensation of aldehydes, malononitrile and C–H-activated acids with a variety of catalysts, such as EDDF-PEG<sub>600</sub>,<sup>[3]</sup> magnetic solid base catalysts,<sup>[4–6]</sup> L-valine,<sup>[7]</sup> H<sub>5</sub>BW<sub>12</sub>O<sub>40</sub>,<sup>[8]</sup> organo-catalysts,<sup>[9,10]</sup> hexamethylenetetramine,<sup>[11]</sup> Cu(II) Schiff base complex,<sup>[12]</sup> Cu@KCC-1-NH-CS<sub>2</sub>,<sup>[13]</sup> DAHP,<sup>[14]</sup> and others.<sup>[15–17]</sup> However, most of these protocols suffered from disadvantages such as the stoichiometric use of catalysts, moderate yields, tedious isolation techniques, and catalyst recycle problems. In this regard, the development novel, sustainable and efficient catalytic systems for

4H-pyrans and their derivatives still exists a great demand.

Ionic liquids (ILs), as a charming functional material, have found various industrial applications in synthesis and catalysis due to their negligible vapour pressure, thermal and chemical stability, non-flammable, nonvolatile and strong structural design prospects.<sup>[18–24]</sup> Through the functional design of anions and cations of ionic liquids, the use of ILs as catalysts in the efficient synthesis of 4H-pyrans and their derivatives have been developed.<sup>[25–27]</sup> However, the isolation of pure ILs from products and reusability has been the major issue in these processes in view of eco-sustainability. Therefore, the immobilization of these functionalized ILs over different solid supports to explore heterogeneous supported ILs has made the process easier through their easy handling, thermal stability, facile isolation and reusability.<sup>[28–32]</sup> Among these solid supports, mesoporous materials offer significant advantages of large surface area, highly ordered structure, thermal and chemical stabilities. These materials can be used as a platform for the loading



**Scheme 1.** Simplified schematic diagram for catalytic synthesis of 2-amino-3-cyano-4H-pyrans.

and dispersion of active components such as ILs or transition metals, thereby increasing their catalytic activities and have been widely utilized as supports in the case of heterogeneous catalysis.<sup>[33–38]</sup> In this work, we wish to report the design and synthesis of a series of mesoporous KIT-6 supported ionic liquids. These supported ionic liquids have been employed as recyclable and high-efficient heterogeneous catalysts for the product of 2-amino-3-cyano-4H-pyrans under mild conditions (Scheme 1). Furthermore, the recycling performance of catalyst and possible catalytic mechanism were explored.

## EXPERIMENTAL

### General

Pluronic 123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) was purchased from Sigma-Aldrich, and other reagents were of analytical grade and used without any further purification. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were carried out on a JSM-7500F electron microscope. FT-IR spectra were recorded on a PE Fourier Transform spectrometer. Powder X-ray diffraction (XRD) data were obtained using Ultima IV diffractometer. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449 F5 at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. UV-Vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. N<sub>2</sub> adsorption–desorption isotherms were recorded using a BELSORP-max instrument and pore size distribution curves were calculated from the analysis of

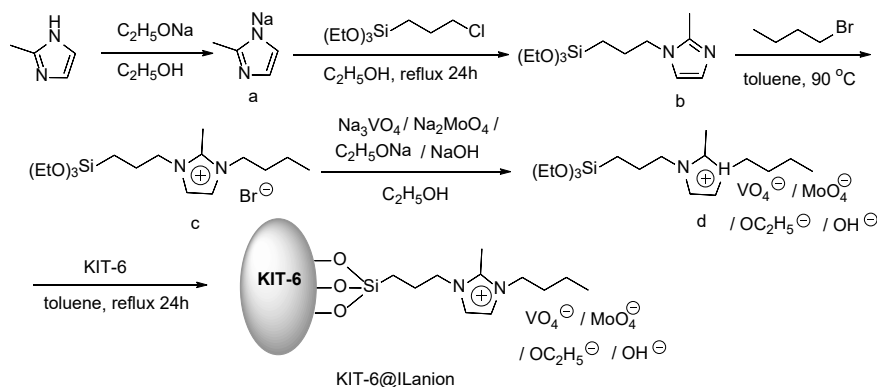
desorption branch of the isotherm by the BJH (Barrett–Joyner–Halenda). NMR spectra were recorded on a Bruker 400 MHz spectrometer. Elemental analysis was recorded on a Vario Micro cube Elemental Analyzer. Melting points were measured by an electro-thermal IA 9100 apparatus.

### Synthesis of Supported Ionic Liquids

KIT-6 was synthesized as described in literatures.<sup>[34–37]</sup> The supported ILs catalysts were synthesized according to literatures (Scheme 2).<sup>[18,19,28–30]</sup> A typical procedure was as follows: Sodium ethoxide (0.5 mol), ethanol (300 mL) and 2-methylimidazole (0.5 mol) were stirred at 80 °C for 5 h to give **a**. Then (3-chloropropyl) triethoxysilane (0.5 mol) was added, and the reaction mixture was refluxed for 24 h. After evaporating the solvent, the mixture was washed with ethanol-water (*v/v* = 1/1, 60 mL) and dried under vacuum to afford **b**. Subsequently, 1-bromobutane (0.3 mol), and **b** (0.3 mol) were added to a 500 mL round-bottomed flask in the presence of toluene (250 mL). The reaction mixture was heated to 90 °C under nitrogen for 24 h, thereafter, the solvent was isolated and dried to give **c**. Next, **c** (0.1 mol), sodium vanadate or sodium molybdate or sodium ethoxide or sodium hydroxide (0.1 mol), ethanol (80 mL) were stirred at 80 °C for 24 h, then the solvent was evaporated, the obtained residue was washed with ethyl acetate and then dried at 50 °C under vacuum to give ionic liquid **d** ILVO<sub>4</sub> or ILMoO<sub>4</sub> or ILOC<sub>2</sub>H<sub>5</sub> or ILOH. Finally, KIT-6 (1.0 g) and **d** (0.4 g) were added into a solution of dry toluene (120 mL), and the mixture was stirred and refluxed for 24 h under nitrogen. Then the resulting solid was filtered, cleansed twice with diethyl ether and dried under vacuum under the temperature of 60 °C for obtaining the supported ILs **e**.

### Catalytic Synthesis of 2-Amino-3-cyano-4H-pyrans

The catalytic synthesis of 2-amino-3-cyano-4-aryl-4H-pyrans were conducted in a 250 mL three-neck flask. In a



**Scheme 2.** Schematic diagram of supported ionic liquids fabrications.

typical procedure, aldehyde (0.01 mol), malononitrile (0.01 mol), ethyl acetoacetate (0.01 mol), EtOH/H<sub>2</sub>O ( $v/v = 1/1$ , 15 mL) and KIT-6@ILMoO<sub>4</sub> (0.5 g) were put into the reactor. And then, the reaction mixture was stirred at 80 °C for a period of time. After completion (by TLC, ethyl acetate / petroleum ether = 1 / 3 solvent system), the mixture was filtered to separate the catalyst and washed with ethanol. The filtrate was concentrated and the crude product purified with ethanol to afford the final product. Fresh substrates were then recharged to the recovered catalyst and then recycled under identical reaction conditions.

### Spectroscopic Data for Products

Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (Table 2, entry 1): White solid, mp 195.7–196.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.19$ – $7.31$  (m, 5H, Ar-H), 4.45 (s, 2H, NH<sub>2</sub>), 4.03 (s, 1H, CH), 2.38 (q, 2H, OCH<sub>2</sub>), 1.58 (s, 3H, CH<sub>3</sub>), 1.09 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 166.7$ , 157.8, 156.6, 142.9, 129.1, 128.2, 127.1, 118.5, 107.5, 62.1, 60.5, 37.8, 18.6, 13.9 ppm; Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 67.57; H, 5.63; N, 9.82; O, 16.84. Found: C, 67.59; H, 5.67; N, 9.85; O, 16.88.

Ethyl 6-amino-5-cyano-2-methyl-4-(p-tolyl)-4H-pyran-3-carboxylate (Table 2, entry 2): White solid, mp 181.0–182.3 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.18$ – $7.74$  (m, 4H, Ar H), 5.25 (s, 1H, CH), 4.72 (s, 2H, NH<sub>2</sub>), 3.96 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 0.99 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.4$ , 157.6, 149.7, 140.1, 134.9, 129.7, 128.5, 118.9, 108.7, 61.9, 60.8, 34.2, 19.5, 18.7, 13.8 ppm; Anal. Calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>: C, 68.41; H, 6.05; N, 9.37; O, 16.06. Found: C, 68.44; H, 6.08; N, 9.39; O, 16.09.

Ethyl 6-amino-5-cyano-2-methyl-4-(o-tolyl)-4H-pyran-3-carboxylate (Table 2, entry 3): White solid, mp 150.5–151.0 °C; <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 7.08$ – $7.14$  (m, 4H, Ar-H), 4.77 (s, 1H, CH), 4.44 (s, 2H, NH<sub>2</sub>), 3.99 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.49 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 1.03 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 165.7$ , 157.4, 149.5, 139.7, 134.6, 130.7, 127.7, 126.3, 124.5, 118.0, 107.6, 61.7, 60.5, 33.9, 19.3, 17.9, 13.6 ppm; Anal. Calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>: C, 68.40; H, 6.03; N, 9.38; O, 16.04. Found: C, 68.44; H, 6.08; N, 9.39; O, 16.09.

Ethyl 6-amino-5-cyano-4-(3-hydroxyphenyl)-2-methyl-4H-pyran-3-carboxylate (Table 2, entry 4): White solid, mp 179.2–180.5 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta = 9.39$  (s, 1H, OH), 7.13–7.16 (m, 1H, Ar-H), 6.91 (s, 2H, NH<sub>2</sub>), 6.59–6.62 (m, 3H, Ar-H), 4.21 (s, 1H, CH), 4.01 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.32 (s, 3H, CH<sub>3</sub>), 1.09 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta = 166.2$ , 158.9, 157.1, 155.8, 145.5, 129.7, 119.3, 118.5, 114.3, 112.4, 107.6, 61.8, 58.6, 39.3, 18.1, 14.2 ppm; Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 63.96; H, 5.35; N, 9.30; O, 21.27. Found: C, 63.99; H, 5.37; N, 9.33; O, 21.31.

Ethyl 6-amino-4-(2-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (Table 2, entry 5): White solid, mp 192.2–193.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.30$ – $7.32$  (m, 1H, Ar-H), 7.16–7.21 (m, 3H, Ar-H), 5.06 (s, 1H, CH), 4.50 (s, 2H, NH<sub>2</sub>), 4.00 (dd, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 1.05 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.8$ , 158.1, 157.9, 141.3, 133.7, 130.5, 129.9, 128.6, 127.4, 118.7, 107.2, 61.3, 60.9, 35.1, 18.5, 13.9 ppm; Anal. Calcd for C<sub>16</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>3</sub>: C, 60.25; H, 4.71; Cl, 11.10; N, 8.77; O, 15.02. Found: C, 60.29; H, 4.74; Cl, 11.12; N, 8.79; O, 15.06.

Ethyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (Table 2, entry 6): White solid, mp 176.0–177.2 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.17$ – $7.23$  (m, 4H, Ar-H), 4.49 (s, 2H, NH<sub>2</sub>), 4.43 (s, 1H, CH), 4.06 (dd, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 1.11 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.7$ , 157.3, 157.1, 143.7, 133.4, 129.5, 128.1, 118.2, 107.6, 61.1, 60.5, 37.2, 18.7, 13.8 ppm; Anal. Calcd for C<sub>16</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>3</sub>: C, 60.24; H, 4.70; Cl, 11.09; N, 8.76; O, 15.03. Found: C, 60.29; H, 4.74; Cl, 11.12; N, 8.79; O, 15.06.

Ethyl 6-amino-5-cyano-2-methyl-4-(2-nitrophenyl)-4H-pyran-3-carboxylate (Table 2, entry 7): Yellow solid, mp 193.0–194.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.80$ – $7.82$  (m, 1H, Ar-H), 7.55–7.57 (m, 1H, Ar-H), 7.35–7.37 (m, 2H, Ar-H), 5.26 (s, 1H, CH), 4.62 (s, 2H, NH<sub>2</sub>), 3.96 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 0.99 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.6$ , 158.7, 158.4, 147.9, 139.4, 133.6, 131.3, 128.1, 124.5, 118.6, 107.4, 61.5, 61.2, 34.2, 18.7, 13.8 ppm; Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>: C, 58.32; H, 4.55; N, 12.74; O, 24.26. Found: C, 58.36; H, 4.59; N, 12.76; O, 24.29.

Ethyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (Table 2, entry 8): Yellow solid, mp 178.0–179.2 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.17$ – $8.20$  (m, 2H, Ar-H), 7.32–7.35 (m, 2H, Ar-H), 4.57–4.60 (d, 3H, NH<sub>2</sub> and CH), 4.05 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.42 (s, 3H, CH<sub>3</sub>), 1.11 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 165.8$ , 158.1, 157.8, 151.6, 146.8, 128.5, 125.2, 118.6, 107.7, 61.1, 60.9, 37.6, 19.2, 14.1 ppm; Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>: C, 58.34; H, 4.51; N, 12.72; O, 24.25. Found: C, 58.36; H, 4.59; N, 12.76; O, 24.29.

Ethyl 6-amino-5-cyano-4-(4-fluorophenyl)-2-methyl-4H-pyran-3-carboxylate (Table 2, entry 9): White solid, mp 165.2–167.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.16$ – $7.19$  (m, 2H, Ar-H), 6.97–6.99 (m, 2H, Ar-H), 4.55 (s, 2H, NH<sub>2</sub>), 4.44 (s, 1H, CH), 4.04 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 1.10 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 166.1$ , 160.4, 156.7, 156.1, 139.8, 130.2, 119.4, 115.3, 107.9, 61.4, 60.7, 38.5, 18.9, 14.4 ppm; Anal. Calcd for C<sub>16</sub>H<sub>15</sub>FN<sub>2</sub>O<sub>3</sub>: C, 63.51; H, 4.97; F, 6.22; N, 9.23; O, 15.85. Found: C, 63.57; H, 5.00; F, 6.28; N, 9.27; O, 15.88.

Ethyl 6-amino-5-cyano-2-methyl-4-(2-(trifluoro-methyl)phenyl)-4H-pyran-3-carboxylate (Table 2, entry 10): White solid, mp 170.4–172.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.55–7.58 (m, 2H, Ar-H), 7.28–7.31 (m, 2H, Ar-H), 4.89 (s, 1H, CH), 4.62 (s, 2H, NH<sub>2</sub>), 3.96 (m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 0.93 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.5, 158.6, 158.1, 144.7, 133.2, 131.9, 128.9, 128.1, 125.5, 123.6, 118.5, 108.3, 61.7, 60.9, 34.3, 19.1, 14.2 ppm; *Anal. Calcd* for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>: C, 57.92; H, 4.26; F, 16.15; N, 7.91; O, 13.60. Found: C, 57.96; H, 4.29; F, 16.18; N, 7.95; O, 13.62.

Ethyl 6-amino-5-cyano-2-methyl-4-(pyridin-4-yl)-4H-pyran-3-carboxylate (Table 2, entry 11): White solid, mp 178.0–179.6 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.53–8.55 (m, 2H, Py-H), 7.14–7.16 (m, 2H, Py-H), 4.73 (s, 2H, NH<sub>2</sub>), 4.44 (s, 1H, CH), 4.05 (dd, 2H, OCH<sub>2</sub>), 2.41 (s, 3H, CH<sub>3</sub>), 1.10 (t, 3H, CH<sub>3</sub>CH<sub>2</sub>O) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.2, 157.9, 157.2, 154.1, 151.2, 122.3, 117.4, 107.3, 61.2, 60.9, 38.1, 18.5, 14.3 ppm; *Anal. Calcd* for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C, 63.11; H, 5.26; N, 14.70; O, 16.78. Found: C, 63.15; H, 5.30; N, 14.73; O, 16.82.

## RESULTS AND DISCUSSION

Initially, the catalytic synthesis of ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate from benzaldehyde, malononitrile, and ethyl acetoacetate was chosen as the model reaction to vary the reaction parameters (Table 1). It can be observed that all the bulk ionic liquids ILVO<sub>4</sub>, ILMoO<sub>4</sub>, ILOC<sub>2</sub>H<sub>5</sub>, ILOH and mesoporous support KIT-6 as catalysts have only 23–81 % product yields after 10–12 h, which suggested that bulk ionic liquids and KIT-6 showed bad catalytic activities (Table 1, entries 5–9). In addition, when catalyst was inexistence, no product was found even at longer reaction time of 24 h (Table 1, entry 10). However, the as-prepared supported ionic liquids could promote the catalytic process significantly, and drastic increase in the product yields were achieved within shorter reaction times of 3–5 h (Table 1, entries 1–4). It was found that the two supported ionic liquids KIT-6@ILMoO<sub>4</sub> and KIT-6@ILOC<sub>2</sub>H<sub>5</sub> demonstrated the better performance, especially KIT-6@ILMoO<sub>4</sub> demonstrated the highest catalytic performance with 93 % product yield (Table 1, entry 2). Next, the effect of amount of best catalyst KIT-6@ILMoO<sub>4</sub> was studied. The product yield increased significantly when the catalyst amount was increased, moderate to excellent yields were obtained from 0.1 g to 0.5 g (Table 1, entries 11–13 and 2), which means that increase of the amount of catalyst is conducive for the condensation reaction. However, the amount of catalyst was further increased to 0.6 g, no obvious enhancement of product yield was observed (Table 1, entry 14). The results showed that KIT-6@ILMoO<sub>4</sub> has the highest catalytic activity with 0.5 g catalyst amount.

**Table 1.** Catalyst screening for synthesis of ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate.<sup>(a)</sup>

Entry	Catalyst	Catalyst / g	Time / h	Yield <sup>(b)</sup> / %
1	KIT-6@ILVO <sub>4</sub>	0.5	5	78
2	KIT-6@ILMoO <sub>4</sub>	0.5	3	93
3	KIT-6@ILOC <sub>2</sub> H <sub>5</sub>	0.5	3	90
4	KIT-6@ILOH	0.5	5	70
5	ILVO <sub>4</sub>	0.5	12	65
6	ILMoO <sub>4</sub>	0.5	10	81
7	ILOC <sub>2</sub> H <sub>5</sub>	0.5	12	76
8	ILOH	0.5	12	58
9	KIT-6	1.0	12	23
10	–	0	24	0
11	KIT-6@ILMoO <sub>4</sub>	0.1	8	48
12	KIT-6@ILMoO <sub>4</sub>	0.3	5	72
13	KIT-6@ILMoO <sub>4</sub>	0.4	3	87
14	KIT-6@ILMoO <sub>4</sub>	0.6	3	93

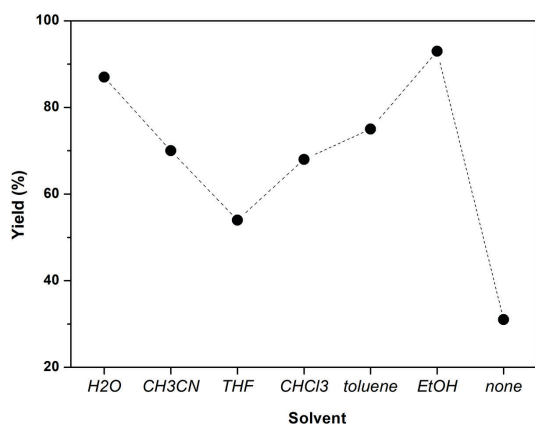
<sup>(a)</sup> The reaction was carried out with benzaldehyde (0.01 mol), malononitrile (0.01 mol), ethyl acetoacetate (0.01 mol), and EtOH (15 mL) at 80 °C.

<sup>(b)</sup> Isolated yield.

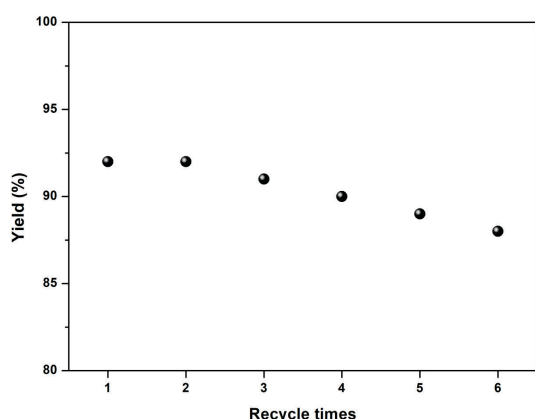
The effect of solvents was performed in the presence of KIT-6@ILMoO<sub>4</sub> at 80 °C (Figure 1). Solvent variations indicated that ethanol were generally better than other solvents such as water, acetonitrile, tetrahydrofuran, trichloromethane, and toluene, with ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate being the best yield. A control experiment showed that solvent-free condition was indispensable for the reaction. It clearly illustrated that ethanol is a more effective solvent. The important indicator to measure the pros and cons for the design of catalyst is the stability evaluation of the catalyst KIT-6@ILMoO<sub>4</sub>. As shown in Figure 2, recycling catalytic experiments over KIT-6@ILMoO<sub>4</sub> were carried out using the model reaction under the optimized conditions. The catalyst KIT-6@ILMoO<sub>4</sub> was easily isolated by filtration and can be used directly for consecutive runs. Remarkably, KIT-6@ILMoO<sub>4</sub> possessed a good reusability and maintained high catalytic performance at least six times without considerable reduction in catalytic activity. The product yield in the six run was 88 %, showing merely a 5 % decrease in performance compared to the fresh catalyst. The recovered catalyst after six times has no obvious change in morphology (Figure S3f). The recovered catalyst after six times has no obvious change in crystalline structure, referring to the XRD pattern in comparison with the fresh catalyst (Figure 3). Furthermore, a hot-filtration test was carried out to investigate the stability of catalyst. The reaction was performed for first 1.5 h with 68 % yield and then the catalyst was filtered off from the reaction mixture. The above filtrate was continued for another 3.5 h, and no progress

for the reaction was monitored by HPLC (Figure 4). This observation indicated that nearly no active species leach into the reaction mixture and also confirmed the good stability of the catalyst examined by thermogravimetric analysis (Figure S7). Hence, the excellent stability and reusability of KIT-6@ILMoO<sub>4</sub> made it possible for commercial applications.

After having the optimized conditions in hand, we explored the generality of our developed protocol by employing other aldehydes and the corresponding catalytic activities were showed in Table 2. The corresponding 2-amino-3-cyano-4H-pyrans were obtained in good to excellent yields (88 % – 98 %) and conversions (90 % – 99 %) within 4 h. The catalytic activities of aldehydes that contained electron donating groups (Table 2, entries 2–4) were higher than those of other aldehydes. When the structure of substitute containing electron withdrawing groups, it took longer time to satisfy the good yields (Table 2, entries 5–10).

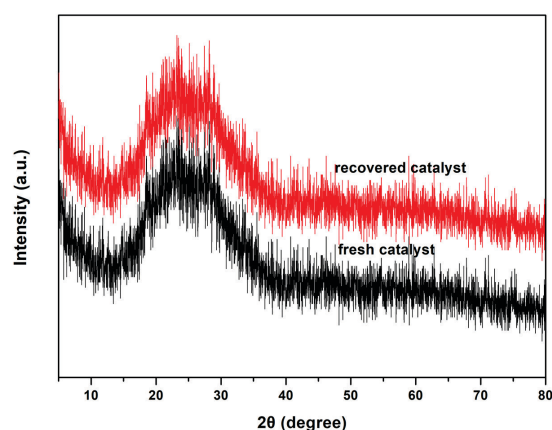


**Figure 1.** Effect of solvent on the reaction. Reaction conditions: benzaldehyde (0.01 mol), malononitrile (0.01 mol), ethyl acetoacetate (0.01 mol), KIT-6@ILMoO<sub>4</sub> (0.5 g), and EtOH (15 mL) at 80 °C.

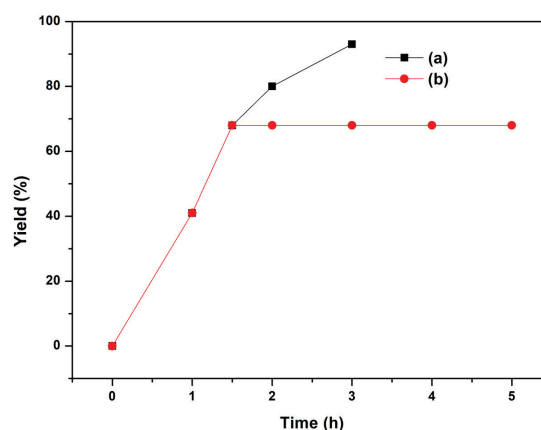


**Figure 2.** Recycling test of reused KIT-6@ILMoO<sub>4</sub>. Reaction conditions: benzaldehyde (0.01 mol), malononitrile (0.01 mol), ethyl acetoacetate (0.01 mol), recovered KIT-6@ILMoO<sub>4</sub> and EtOH (15 mL) at 80 °C.

Based on the above results and relevant literatures,<sup>[8–12]</sup> a possible catalytic mechanism is proposed for this reaction (Scheme 2). The first step involves the Knoevenagel condensation of aldehyde and malononitrile for the formation of the intermediate olefin **I**. The MoO<sub>4</sub> anion of KIT-6@ILMoO<sub>4</sub> activates malononitrile and hydroxyl groups on the SBA-15 support activates aldehyde, which could help to activate the condensation and improves the reaction efficiency. At the same time, the multifunctional catalyst helps to activate ethyl acetoacetate to form the intermediate enolate **II**. Subsequently, the intermediate **II** adds to **I** by Michael addition to give the intermediate **III**, followed by the intramolecular cyclization to give the target compound **IV**. The synergistic effect of Mo O<sub>4</sub> and hydroxyl hydroxyl active species is helpful to the reaction and can greatly accelerate the catalytic performance.



**Figure 3.** XRD patterns of the fresh and recovered KIT-6@ILMoO<sub>4</sub>.



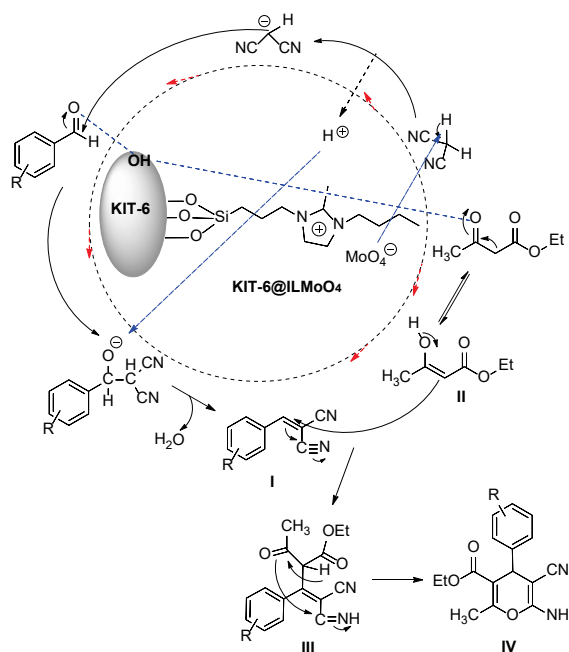
**Figure 4.** Hot filtration test for the reaction. Reaction conditions: benzaldehyde (0.01 mol), malononitrile (0.01 mol), ethyl acetoacetate (0.01 mol), and EtOH (15 mL) at 80 °C with catalyst (a) and catalyst removal (b) after 1.5 h.

**Table 2.** Catalytic synthesis of 2-amino-3-cyano-4H-pyrans.<sup>(a)</sup>

Entry	Substrate	Product	Time / h	Conver- sion / %	Yield <sup>(b)</sup> / %
1			3	94	93
2			2	99	98
3			2	97	96
4			2	97	95
5			4	92	90
6			4	91	91
7			4	90	88
8			4	90	89
9			4	92	91
10			4	91	89
11			3	97	96

<sup>(a)</sup> Reaction conditions: aldehyde (0.01 mol), malononitrile (0.01 mol), ethyl acetoacetate (0.01 mol), KIT-6@ILMoO<sub>4</sub> (0.5 g) were stirred in EtOH (15 mL) at 80 °C.

<sup>(b)</sup> Isolated yield.

**Scheme 3.** Proposed catalytic mechanism.

## CONCLUSIONS

In conclusion, a series of mesoporous KIT-6 supported ionic liquids were prepared and tested as catalysts for the synthesis of 2-amino-3-cyano-4H-pyrans. The experiment demonstrated that the catalyst KIT-6@ILMoO<sub>4</sub> possessing abundant active sites exhibited excellent activity in good to excellent yields (88 % – 98 %), may be attributed to the synergistic effect between hydroxyl groups of support beta and molybdate from the ionic liquid greatly accelerates the reaction. The catalyst having full utilization of active sites can be easily recovered and reused for six times without considerable reduction in catalytic activity. The protocol was found to be advantageous in terms of good to excellent yields, ease of isolation and reusability of the catalyst. This study confirmed that the construction of synergistic catalytic active sites of mesoporous material supported ILs was a cost effective way that not only markedly enhanced the catalytic activity but also facilitated the operation and transport, which offered a broad application prospect in the practical application of green and high efficient catalytic heterogeneous process.

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**Supplementary Information.** Characterization data of supported ionic liquids and products are provided in the supporting information. Supporting information to the paper is attached to the electronic version of the article at: <https://doi.org/10.5562/cca3797>.

PDF files with attached documents are best viewed with Adobe Acrobat Reader which is free and can be downloaded from [Adobe's web site](https://www.adobe.com/acrobat).

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