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## Synthesis and Characterization of Ionic Liquid Based Bifunctional Periodic Mesoporous Organosilica Supported Potassium Carbonate as Very Efficient Nanocatalyst for the Knoevenagel Condensation

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#### Highlights ►

▶ Novel bifunctional ionic liquid based PMO supported  $K_2CO_3$  was prepared and characterized ▶ Excellent properties of this nanomaterial were developed in details ▶ This material was applied as an efficient nanocatalyst for the Knoevenagel reaction ▶ The Knoevenagel products were obtained in high to excellent yields and selectivities ▶ This nanocatalyst was reused several times without important decrease in efficiency ▶ ▶

Graphical abstractA novel ionic liquid based bifunctional periodic mesoporous organosilica supported potassium carbonate was prepared, characterized and its catalytic activity was investigated in the Knoevenagel reaction. This catalyst exhibited high efficiency for the preparation of different derivatives of Knoevenagel products under moderate reaction conditions. Moreover, the catalyst was successfully recovered and reused several times without important decrease in reactivity and stability.

#### Abstract

A novel ionic liquid based bifunctional periodic mesoporous organosilica supported potassium carbonate (BPMO-IL-KCO<sub>3</sub>) is prepared, characterized and its catalytic efficiency is studied in the Knoevenagel reaction. The BPMO-IL-KCO<sub>3</sub> was prepared by chemical attachment of 1-methyl-(3-trimethoxysilylpropyl)imidazolium chloride on an ionic liquid based PMO followed by treatment with potassium carbonate under ambient temperature. This material was characterized with thermal gravimetric analysis (TGA), energy-dispersive X-ray (EDX) spectroscopy, powder X-ray

diffraction (PXRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The BPMO-IL-KCO<sub>3</sub> was then successfully applied as efficient base catalyst in the Knoevenagel condensation of different aldehydes with ethyl cyanoacetate and gave high to excellent yields of the corresponding coupling products. The catalyst was recovered and reused several times without significant decrease in activity and selectivity. The recovered catalyst was also analyzed with TEM and nitrogen sorption experiment to investigate structural stability and durability of the material under applied conditions.

Keywords: Bifunctional PMO• ionic liquid• basic PMO-IL• Knoevenagel condensation• recoverable nanocatalyst

#### **1. Introduction**

The discovery of periodic mesoporous organosilicas (PMOs) with unique physiochemical properties, high loading of organic functional groups in their framework as well as high thermal, mechanical and chemical stability, and their expanding potential applications was a great achievement in the field of material chemistry at last decade [1-3]. PMOs are synthesized by simultaneous hydrolysis and condensation of bridged organosilane precursors in the presence of surfactant template as structure directing agent [3]. To date, different approaches such as the selection of hydrolytic reaction conditions, design of anionic or natural templates, development of new precursors, and the use of co-condensation or grafting manners, have enabled the hierarchical structural control of PMOs from molecular- and meso-scale structures to macroscopic morphology [3]. An interesting success of PMOs that combines the unique framework properties with specific active sites is the making of bifunctional PMOs (BPMOs) containing organic functional moieties both in pore wall and mesochannel [4, 5]. Due to high accessibility and therefore high reactivity of mesochannel groups of BPMOs, they have excellent efficiency especially in the catalytic processes [4, 5]. To date several BPMO materials with diverse

functionality have been prepared and applied as catalyst in different organic reactions [4-6]. As an example, more recently we prepared a new BPMO based on ionic liquid and propylsulfonic acid groups (BPMO-IL-SO<sub>3</sub>H) and studied its catalytic application in the esterification of carboxylic acids and Biginelli reactions [6]. The BPMO-IL-SO<sub>3</sub>H gave well to excellent yield of desired products and could be recovered and reused several times without significant decrease in efficiency, a feature that attributed to the present of imidazolium moiety in the framework of the material [6].

On the other hand, the preparation of substituted alkenes through Knoevenagel reaction is one of the most important organic processes which is very interested in between chemists due to its key role in the production of biologically active compounds and fine chemicals [7, 8]. In the Knoevenagel process, activated methylenes are reacted and condensed with carbonyls in the presence of acid or base catalysts to prepare  $\alpha$ ,  $\beta$ -unsaturated products [7, 8]. Traditionally, a lot of organic and/or inorganic bases such as pyridine, primary, secondary and tertiary amines, KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and K<sub>2</sub>HPO<sub>4</sub> have been widely used as catalyst in the Knoevenagel condensation of a variety of different activated methylenes with carbonyl compounds under homogeneous conditions [7, 9]. This reaction has also extensively been performed in the presence of many homogeneous Lewis acid catalysts such as TiCl<sub>4</sub>, CuCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, LaCl<sub>3</sub> and NbCl<sub>5</sub> [7, 10]. However, since the homogeneous catalytic systems suffer from problems of catalyst recovery, product separation and environmental pollution, therefore, several strategies have been recently developed for the preparation of recoverable heterogeneous catalyst for this important reaction. Along this line, several solid materials supported acid or base catalysts have been prepared for catalyzing Knovenagel condensation under heterogeneous conditions [11-17]. Among different supports applied in this regard, ordered mesoporous silicas are more attracted because of their high specific surface area, high thermal and mechanical stability, uniform pore size distribution and good recoverability [15-17]. Although, these successes have decreased some restrictions related to catalyst recovery and product isolation, however, some limitations including the use of volatile organic solvents, high catalyst loading and high reaction temperature are still observed in these systems. Hence, the development of efficient environmental-friendly catalytic systems, especially metal-free, while

demonstrating excellent reactivity and reusability feature, is still a need for the Knoevenagel condensation. Therefore, herein in continuation of our recent studies in the field of bifunctional PMOs and according to importance of the Knoevenagel condensation in the synthetic organic chemistry, we wish to disclose, for the first time, the preparation and characterization of a novel ionic liquid based bifunctional periodic mesoporous organosilica with basic property (BPMO-IL-KCO<sub>3</sub>) as well as study its catalytic application in the Knoevenagel condensation of different aldehydes with ethyl cyanoacetate at ambient temperature (Scheme 1).

#### 2. Experimental

#### 2.1. Preparation of BPMO-IL-KCO<sub>3</sub> nanocatalyst:

Firstly, the 1-methyl-(3-trimethoxysilylpropyl)imidazolium chloride ionic liquid was prepared by reaction of *N*-methylimidazole (5 mmol) and 3-chloropropyl-trimethoxysilane (5 mmol) in toluene under reflux conditions during 30 h [18]. The PMO-IL nanomaterial (see Supporting Information) was then reacted with a substoichiometric amount of 1-methyl-(3-trimethoxysilylpropyl)imidazolium chloride *via* a grafting approach to give ionic liquid based bifunctional PMO (BPMO-IL-Cl). Ionic liquid based bifunctional PMO with basic property (BPMO-IL-KCO<sub>3</sub>) was then prepared by treatment of BPMO-IL-Cl with potassium carbonate (Scheme 1). For this, the BPMO-IL-Cl (1g) was added to a flask containing distilled water (50 mL) and vigorously stirred at room temperature. After complete dispersion of BPMO-IL-Cl in water, potassium carbonate (5 mmol) was filtered and completely washed with distilled water to remove KCl and unreacted potassium carbonate. The final material was dried for 12 h at 70 °C and gave a white powder denoted as KCO<sub>3</sub>-containing ionic liquid based bifunctional PMO (BPMO-IL-KCO<sub>3</sub>). The loading of the KCO<sub>3</sub> was obtained to be 1.2 mmol/g by the means of the potassium content obtained from energy-dispersive X-ray (EDX) spectroscopy.

# 2.2. General procedure for the preparation of Knoevenagel products using BPMO-IL-KCO<sub>3</sub> nanocatalyst

For this, BPMO-IL-KCO<sub>3</sub> nanocatalyst (0.5 mol %) was added to a flask containing a homogeneous ethanol solution of aldehyde (2 mmol) and ethyl cyanoacetate (2.2 mmol). The obtained mixture was then magnetically stirred at 50 °C for an appropriate time indicated in Table 2. The reaction progress was monitored by TLC. After completion of the reaction, warm ethanol (8 mL) was added and the reaction mixture was separated from the catalyst by filtration and washing with ethanol. Pure products were obtained after recrystallization in a mixture of hexane/ethanol solvent or isolated the residue by column chromatography on silica.

# 2.3. General procedure for the recovery of BPMO-IL-KCO<sub>3</sub> nanocatalyst in the Knoevenagel reaction

For this, aldehyde (5 mmol), ethyl cyanoacetate (5.5 mmol) and BPMO-IL-KCO<sub>3</sub> nanocatalyst (0.5 mol %) were added to ethanol and the mixture was magnetically stirred at 50 °C. The reaction progress was monitored by TLC. After the reaction was completed, warm ethanol (10 mL) was added and the obtained solution was hotly filtered. The catalyst was separated from reaction mixture by further washing with warm ethanol. Then this nanocatalyst was reused at the same conditions as the first run for at least 7 times and gave corresponding Knoevenagel product in high yield and selectivity (Table 3).

#### 2.4. General procedure for the hot filtration test in the Knoevenagel reaction

The hot filtration test was carried out in the reaction of benzaldehyde (2 mmol) with ethyl cyanoacetate (2.2 mmol) in the presence of 0.5 mol % of catalyst in EtOH at 50 °C. After about 50 % of the reaction was progressed, the obtained mixture was hotly filtered. The filtrate was then allowed to continue under optimized conditions during 3 h and the reaction progress was monitored.

#### 3. Results and Discussion

The ionic liquid based periodic mesoporous organosilica (PMO-IL) was first prepared according to our recently reported procedure with a slight modification [18]. The PMO-IL nanomaterial was then reacted with a substoichiometric amount of 1-methyl-(3-trimethoxysilylpropyl)imidazolium chloride *via* a grafting approach to give ionic liquid based bifunctional PMO (BPMO-IL-Cl). Next, the BPMO-IL-Cl was treated with potassium carbonate to produce bifunctional PMO-IL with basic property (BPMO-IL-KCO<sub>3</sub>, Scheme 1). The BPMO-IL-KCO<sub>3</sub> nanomaterial was then characterized with several techniques such as nitrogen adsorption-desorption experiment, powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), and energy-dispersive X-ray (EDX) spectroscopy.

Nitrogen adsorption-desorption analysis of the BPMO-IL-KCO<sub>3</sub> exhibited typically type IV isotherm and H1 hysteresis loop with a relatively sharp capillary condensation step at a relative pressure of approximately 0.70, and a very sharp capillary evaporation step centered at approximately 0.5 (Figure 1a). The BET surface area and total pore volume of the material were also found to be 523  $m^2/g$  and 0.92 cm<sup>3</sup>/g, respectively. The average pore diameter of BPMO-IL-KCO<sub>3</sub>, calculated using the Barrett-Joyner-Halenda (BJH) method, showed a sharp pore-size distribution centered at 7.2 nm (Figure 1b). These data successfully confirm the presence of a two dimensional (2D) hexagonal mesopore structure with a narrow pore-size distribution for the material. Powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) analyses of the BPMO-IL-KCO<sub>3</sub> were carried out to get insight into the structural feature of the material. The PXRD pattern of the catalyst illustrated one peak with high intensity at 2 $\Theta$  of 1 degree corresponding to d100 reflection and two peaks with low intensity at 2 $\Theta$  of 1.62 and 1.84 corresponding, respectively, to d110 and d200 reflections. These strongly confirm the presence of highly ordered mesostructure with two-dimensional hexagonal symmetry (p6mm) lattice for the material (Figure 2). TEM image was in good agreement with the results of PXRD analysis and also showed well ordered two-dimensional mesochannels for the material (Figure 3). The scanning electron microscopy (SEM) image of the BPMO-IL-KCO<sub>3</sub> was next carried out to show the morphology of the material (Figure 4). This demonstrated a uniform and regular rope-like morphology for the material

surface. Thermal gravimetric analysis (TGA) of the material was also carried out to study the thermal stability of the material (Figure 5). The first weight loss (4.69 %) in the temperature below 120 °C is corresponded to removal of physosorbed water and alcoholic solvents remained from synthesis process. The second weight loss (1.24 %) between 120 and 220 °C is attributed to elimination of surfactant template, remained from extraction process. The third and main weight loss from 250 to 600 °C (23.82 %) is corresponded to methyl-propyl-imidazolium ionic liquids grafted onto solid surface and also bis(propyl) imidazolium ionic liquids incorporated in the material pore wall. These observations confirm successful immobilization and incorporation of ionic liquid moieties into/onto material network.

Energy-dispersive X-ray (EDX) spectroscopy of the BPMO-IL-KCO<sub>3</sub> was carried out to be evidence for the presence of C, O, Si, N and K in the material (Figure 6). The elemental distribution mapping of this analysis demonstrated signals of carbon, oxygen, silicon, nitrogen and potassium in the sample. This successfully confirms well immobilization and/or incorporation of ionic liquid and potassium carbonate moieties onto/into material network. Importantly, the signal of chlorine should be observed at 2.65 KeV [3e], however, this was not seen in the EDX spectrum of the BPMO-IL-KCO<sub>3</sub> material confirming successful replacement of chloride anions with KCO<sub>3</sub> during anion exchange process.

After characterization, the catalytic application of BPMO-IL-KCO<sub>3</sub> was investigated in the Knoevenagel condensation of aldehydes with ethyl cynoacetate under different conditions. Firstly, the effect of solvent and catalyst loading was investigated in the condensation of benzaldehyde with ethyl cyanoacetate, as a model reaction, at 50 °C (Table 1). The results showed that in toluene low yield of Knoevenagel product was obtained, while CH<sub>3</sub>CN and H<sub>2</sub>O delivered good yield of desired product. Interestingly, in EtOH an excellent yield was obtained under the same conditions as before (Table 1, entries 1-4). The study also showed that the reaction was strongly affected by the amount of the catalyst. As shown in Table 1, by increasing the amount of catalyst from 0.15 to 0.5 mol% a significant increase in the yield is observed (Table 2, entries 4–7), and the best result is obtained in the presence of 0.5 mol% of catalyst. To show the impact of chemically grafted ionic liquid groups in the catalytic process, in the

next study the catalytic efficiency of PMO-IL-KCO3 was checked under the same reaction conditions as BPMO-IL-KCO<sub>3</sub> (Table 1, entry 4 vs. entry 8). Attractively, in the later case only 58 % of the Knoevenagel product was obtained indicating the key role of grafted IL moieties in the catalytic process. This result may be attributed to better accessibility and flexibility of highly active catalytic sites, [methyl-propylimidazolium][KCO<sub>3</sub>] moieties, of BPMO-IL-KCO<sub>3</sub> in comparison with PMO-IL-KCO<sub>3</sub>. In another study the BPMO-IL-OH nanocatalyst was prepared by treatment of potassium hydroxide with BPMO-IL using the same procedure as BPMO-IL-KCO<sub>3</sub>. Comparative efficiency tests were then performed on BPMO-IL-KCO3 and BPMO-IL-OH catalysts in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate under the same conditions (Table 1, entry 4 vs. entry 9). Interestingly, at the same reaction time as BPMO-IL-KCO<sub>3</sub>, BPMO-IL-OH gave 69% yield of the desired product confirming that the efficiency of KCO<sub>3</sub>-containing BPMO-IL is much better than those of hydroxyl-containing BPMO-IL. With the optimum conditions in hand, the scope and limitation of this catalyst was next investigated in the Knovenagel condensation of various aldehydes with ethyl cyanoacetate (Table 2). As mentioned above, benzaldehyde delivered excellent yield of corresponding substituted alkene at 50 °C and short reaction time (Table 2, entry 1). The catalyst also demonstrated excellent activity for other aromatic aldehydes bearing both electron donating and electron withdrawing substituents (Table 2, eateries 2-12). As shown, 2-methyl-benzaldehyde, 4-methyl-benzaldehyde, 4methoxy-benzaldehyde, 4-hydroxy-benzaldehyde and 3-ethoxy-4-hydroxy-benzaldehyde (Table 2, entries 2-6) delivered corresponding products in high yields (Table 2, entries 2-6). The electron withdrawing groups containing aldehydes such as 2-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-3-bromobenzaldehyde, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde also chlorobenzaldehyde, afforded desired adducts in excellent yields (Table 2, entries 7-12). Importantly, the catalyst also showed high efficiency for the less reactive orth-substituted benzaldehydes such as 2-methyl-benzaldehyde (Table 2, entry 2) and 2-chlorobenzaldehyde (Table 2, entry 7). Interestingly, aliphatic aldehydes such as butyl aldehyde and acetaldehyde also delivered good yield of the corresponding alkene products under the same conditions as above (Table 2, entries 13, 14). These results successfully illustrate the high

performance of the designed catalyst for the preparation of a wide range of substituted alkenes which are important intermediates in the field of pharmacology and chemistry.

The recoverability and reusability of the catalyst was then examined by carrying out runs of the reaction with the same batch of the catalyst in the model reaction between benzaldehyde and ethyl cyanoacetate. In order to regenerate the catalyst after each cycle, it was separated and washed completely with ethanol and dried under vacuum at 70 °C. This was then applied in aforementioned reaction under conditions as before. Interestingly, the result illustrated that the catalyst could be recovered and reused at least 7 times with remaining its efficiency (Table 3). Moreover, according to the elemental analysis, no significant decrease of the K-loading in the recovered catalyst was detected after used, indicating that the leaching of basic active sites could be essentially neglected.

To further investigate whether the catalyst works in a homogeneous or heterogeneous manner, a hot filtration test was carried out in the reaction of benzaldehyde with ethyl cyanoacetate as a test model. For this, after about 50 % of the reaction was progressed, the obtained mixture was hotly filtered. The filtrate was then allowed to continue under optimized conditions. Importantly, no considerable reaction progress was observed after 3 h. These observations verify that the leaching of KCO<sub>3</sub> species were negligible under applied conditions and the catalyst was most likely operating in a heterogeneous manner. The recovered catalyst after fifth reaction cycle was analyzed by nitrogen-sorption experiment and TEM analysis to investigate the structural and chemical stability of the material under applied conditions. The TEM image of the recovered catalyst clearly demonstrated that the BPMO-IL-KCO<sub>3</sub> catalyst remained well-defined ordered mesoporous structure after being reused for 4 times (Figure 7). Moreover, the nitrogen adsorption-desorption and BJH pore size isotherms of the recovered BPMO-IL-KCO<sub>3</sub> illustrated a pattern the same as fresh catalyst (Figure 8). As shown the nitrogen-sorption illustrated a type IV isotherm with H1 hysteresis loop. The BET surface area and mean pore volume of this were decreased to  $408 \text{ m}^2/\text{g}$  and  $0.84 \text{ cm}^3/\text{g}$ , respectively (Table 1S). The BJH pore size distribution

also showed a peak with good density centered at 7.1 (Figure 8b, Table 1S). These observations exhibit high hydrothermal, mechanical and chemical stability of the catalyst during applied conditions.

#### 4. Conclusions

In conclusion, for the first time, a novel ionic liquid based bifunctional periodic mesoporous organosilica with basic property (BPMO-IL-KCO<sub>3</sub>) was prepared, characterized and applied as effective heterogeneous nanocatalyst in the Knoevenagel condensation. The powder X-ray diffraction, transmission electron microscopy and nitrogen sorption analyses confirmed that the material had a wellordered two-dimensional hexagonal symmetry. The TG analysis showed high thermal stability of well incorporated ionic liquid moieties in the material. Energy-dispersive X-ray analysis successfully proved well immobilization and/or incorporation of ionic liquid and potassium carbonate moieties onto/into material framework. The catalyst was effectively used in the Knoevenagel condensation of aldehydes with ethyl cyanoacetate and afforded corresponding substituted alkenes in high to excellent yield. The catalyst was also recovered and reused at least seven times without significant decrease in efficiency. TEM image of the recovered BPMO-IL-KCO<sub>3</sub> after fifth reaction cycle showed the presence of wellordered 2-dimensional hexagonal mesochannels indicating high chemical and structural stability of the material under applied conditions. Other advantages of this study include mild reaction conditions, high yield of products as well as high activity, stability and durability of the catalyst during reaction process. According to abovementioned advantages, some applications of the BPMO-IL-KCO<sub>3</sub> in the other base catalyzed organic processes are underway in our laboratory.

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Scheme and Figure captions:

Scheme 1. Preparation of BPMO-IL-KCO3 nanocatalyst and its application in the Knoevenagel reaction

Figure 1. Nitrogen adsorption-desorption (a) and BJH pore size distribution (b) isotherms of the

BPMO-IL-KCO3 nanocatalyst

Figure 2. Powder X-ray diffraction (PXRD) pattern of the BPMO-IL-KCO<sub>3</sub> nanocatalyst

Figure 3. TEM image of the BPMO-IL-KCO<sub>3</sub> nanocatalyst

Figure 4. SEM image of the BPMO-IL-KCO<sub>3</sub> catalyst

Figure 5. Thermal gravimetric analysis of the BPMO-IL-KCO<sub>3</sub> nanocatalyst

Figure 6. Energy-dispersive X-ray (EDX) of the BPMO-IL-KCO3

Figure 7. TEM image of the recovered BPMO-IL-KCO<sub>3</sub> after fifth reaction cycle

Figure 8. Nitrogen adsorption-desorption (a) and BJH pore size distribution (b) isotherms of the

recovered BPMO-IL-KCO3 nanocatalyst after fifth cycle

<b>Table 1.</b> The effect of the kind of catalyst, solvent and catalyst loading in the Knoevenagel condensation of ethyl cynoacetate with benzaldehyde <sup>[a]</sup>				
$ \begin{array}{c} O \\ H \\ + \\ \end{array} \\ O \\ O \\ O \\ O \\ C \\ C \\ C \\ C \\ C \\ C$				
Entry	Catalyst	Catalyst loading (mol %)	Solvent	Yield $(\%)^{[b]}$
1	BPMO-IL-KCO <sub>3</sub>	0.5	Toluene	37

2	BPMO-IL-KCO <sub>3</sub>	0.5	H <sub>2</sub> O	78
3	BPMO-IL-KCO <sub>3</sub>	0.5	CH <sub>3</sub> CN	75
4	BPMO-IL-KCO <sub>3</sub>	0.5	EtOH	96
5	BPMO-IL-KCO <sub>3</sub>	0.4	EtOH	75
6	BPMO-IL-KCO <sub>3</sub>	0.3	EtOH	57
7	BPMO-IL-KCO <sub>3</sub>	0.15	EtOH	26
8	PMO-IL- KCO <sub>3</sub>	0.5	EtOH	58
9	BPMO-IL-OH	0.5	EtOH	69
<sup>[a]</sup> Reaction conditions: Benzaldehyde (2 mmol), ethyl cyanoacetate (2.2 mmol), solvent (5 mL), 50 °C, 80 min. <sup>[b]</sup> Isolated yields.				

**Table 2.** The Knoevenagel condensation of aldehydes with ethyl cyanoacetate in the presence of BPMO -IL-KCO<sub>3</sub> nanocatalyst<sup>[a]</sup>



Entry	Aldehyde	Time (min)	Yield (%) <sup>[b]</sup>	TON <sup>[c]</sup>
1	PhCHO	80	96	192
2	2-Me-PhCHO	100	85	170
3	4-Me-PhCHO	88	90	180
4	4-MeO-PhCHO	100	90	180

5	4-OH-PhCHO	100	88	176
6	3-EtO, 4-OH-	100	86	172
	PhCHO			
7	2-Cl-PhCHO	100	90	180
8	3-Cl-PhCHO	90	95	190
9	4-Cl-PhCHO	85	94	188
10	3-Br-PhCHO	90	92	184
11	3-NO <sub>2</sub> -PhCHO	30	95	190
12	4-NO <sub>2</sub> -PhCHO	30	97	194
13	Butylaldehyde	105	75	150
14	Acetaldehyde	105	74	148
<sup>[a]</sup> Reaction conditions: Aldehyde (2 mmol), ethyl cyanoacetate (2.2 mmol), catalyst (0.5				

mol%), EtOH (5 mL), 50 °C. <sup>[b]</sup> Isolated yields. <sup>[c]</sup> TON = turnover number (defined as mmol of product/mmol of catalyst).

**Table 3.** Reusability of the BPMO-IL-KCO $_3$  catalyst in the Knoevenagel reaction ofbenzaldehyde with ethyl cyanoacetate

Run	Time (min)	Yield (%)	TON
1	80	96	192
2	80	96	192
3	90	92	184
4	90	92	184
5	95	88	176
6	95	90	180
7	100	88	176

8	100	86	172