ORIGINAL PAPER



# Star-like polyionic heterogeneous nanocatalyst as a highly active catalyst for promotion of Baylis–Hillman reaction in [bmim]Cl

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**Abstract** The use of star-like polyionic Lewis base heterogeneous nanocatalyst for the Baylis–Hillman reaction of benzyl- and methylacrylates with aryl aldehydes has been investigated. The corresponding Baylis–Hillman adducts are obtained in good to high yields in one-pot procedure at room temperature in 5.5–8 h. The catalyst can be easily recovered with excellent purity by filtration and can be reused directly without any change in its catalytic activity.

**Keywords** Baylis–Hillman reaction · Star-like polyionic compound · Heterogeneous nanocatalyst

### Introduction

Baylis–Hillman reaction is one of the many important carbon–carbon bond-forming reactions which have been used for the synthesis of natural products and biologically active compounds [1–4]. Densely functionalized carbon skeleton synthesis from the simple readily available  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds and aldehydes in the presence of a Lewis base catalyst is one of the significances of this transformation. Despite great developments in this reaction, including development of a catalytic, asymmetric version and aza-Baylis–Hillman reactions, the need for alternative methods for the preparation of these novel synthesis is still of great interest [5–9]. In general, small Lewis base molecules, such as DABCO, DMAP, DBU, PPh<sub>3</sub>, PBu<sub>3</sub> or PPh<sub>2</sub>Me, which are difficult to isolate from the reaction solution and reuse, have been used as the promoters in the Baylis–Hillman reaction [10, 11]. Using of recyclable catalyst has become the key factor for a chemical reaction to be an economical, safe, environmentally benign, resourceand energy-saving process [12]. It is very clear that if we can design and synthesize a recyclable Lewis base as a promoter for the Baylis–Hillman reaction, this would be accomplished in a perfect atom-economic way.

Room temperature ionic liquids (ILs) have attracted much attention in organic chemistry as reaction solvents and catalysts (for reviews, see [13–15]), due to their low volatility and many other advantages. Great rate accelerations or good selectivity have been reported in the presence of ILs [16]. However, in some cases, product and catalyst isolation can be difficult in ILs [17]. Noting that Baylis-Hillman reaction was accelerated in the presence of ILs [18], we speculated that the Lewis base-tethered polyionic compound can catalyze this reaction. Very recently, we synthesized nitrite-functionalized star-like polyionic heterogeneous nanocatalyst and used as a nitrosonium source and catalyst for the synthesis of azo dyes under solvent-free conditions [19]. In this study, we synthesized Lewis basetethered star-like polyionic compound and investigated its effect on Baylis-Hillman reactions of benzyl- and methyl acrylates with aryl aldehydes in [bmim]Cl at room temperature (Scheme 1).

### **Experimental**

#### Materials and instrumentation

All reagents were purchased from Merck Company and used without further purification. Infrared spectra

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Scheme 1 Star-like polyionic Lewis base heterogeneous nanocatalyst for promotion of Baylis–Hillman reaction



were recorded in KBr and determined on a Perkin Elmer FT-IR spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance AC-300 MHz using CDCl<sub>3</sub> as the deuterated solvent and TMS as the internal standard. The morphology of the catalyst was studied by field emission scanning electron microscopy (FESEM; Hitachi, model S-4160), and the structure of the catalyst was confirmed by energy-dispersive X-ray analysis (EDX; Tescan; model MIRA3FEG-SEM) and elemental analysis (CHNS; Euro EA; model EA2000).

### Synthesis of silica nanoparticles

Ammonia solution 25 % (750  $\mu$ L, 10 mmol) and water (1.98 mL) were added into a 250 mL round-bottom flask containing absolute methanol (100 mL). The solution was stirred for 10 min at room temperature. While stirring of the solution, tetraethoxysilane (11 ml, 50 mmol) was added dropwise. The final solution was stirred continuously for 3 days at ambient temperature. The particle size was examined under scanning electron microscopy. FT-IR (KBr, cm<sup>-1</sup>): 3456 (Si–OH), 1639, 1097 (SiO–H), 803 (Si–OH).

### Synthesis of star-like polyionic Lewis base nanocatalyst

3-Chloropropyltrimethoxysilane (1.82 ml, 10 mmol) was reacted with N,N,N',N'-tetramethylethylenediamine (1.94 ml, 13 mmol) in acetonitrile (5 mL) for 3 days at 80 °C to provide the ionic liquid 6. After completion of the reaction, acetonitrile was evaporated and unreacted diamine was extracted using dichloromethane, and the crude ionic liquid 6 was achieved. Then, ionic liquid 6 was immobilized on the freshly prepared nanosilica by stirring of these two compounds in acetonitrile at 60 °C for 3 days to produce the ionic liquid-immobilized nanosilica 7. As shown in Scheme 1, successive reactions of compound

7 with 1,4-dichlorobutane and then with *N*,*N*,*N'*,*N'*-tetramethylethylenediamine were carried out to produce the desired star-like polyionic Lewis base heterogeneous nanocatalyst 11. At the end of the reaction, the mixture was stirred vigorously in acetonitrile at 40 °C for 3 h and then centrifuged to provide the crude catalyst 11. FT-IR (KBr, cm<sup>-1</sup>): 3442 (Si–OH), 2958 (C–H), 1638 (O–H), 1486 (C–H), 1093 (asymmetric Si–O), 957 (asymmetric Si–OH), 800 (symmetric Si–O); EDX: Calcd.: N/C (%w) = 0.241; Found (%): C, 9.47; N, 2.33; O, 46.49; Si, 40.43; Cl, 1.27. N/C (%w) = 0.246; Anal. Calcd. Found (%): C, 17.76; N, 4.37; H, 4.24. N/C (%w) = 0.246.

# General procedure for the Baylis–Hillman adducts using star-like polyionic catalyst 11

Benzaldehyde derivative (10 mmol) and benzylacrylate (10 mmol) or methylacrylate (10 mmol) were added to a vessel containing [bmim]Cl (3 mL). Then, catalyst 11 was added and the mixture was stirred at room temperature for the times as shown in Table 3. After completion of the reaction, the products were isolated and purified by column chromatography using ethyl acetate/*n*-hexane as eluent.

### Spectroscopic and analytical data

### Benzyl 2-(hydroxy(4-nitrophenyl)methyl)acrylate (3a)

FT-IR (KBr, cm<sup>-1</sup>): 3480, 2986, 1719, 1629, 1606, 1520, 1348, 1245. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.15 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.24-7.12 (m, 5H), 6.54 (s, 1H), 5.89 (s, 1H), 5.59 (s, 1H), 5.11 (s, 2H), 3.37 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  165.61, 148.67, 147.31, 141.16, 135.11, 128.51, 128.40, 128.10, 127.37, 127.22, 123.46, 72.22, 66.77. Anal. Calc. for

C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>: C 65; H 4.79; N 4.47 %. Found: C 64.88; H 4.65; N 4.59 %.

# Benzyl 2-((4-cyanophenyl)(hydroxy)methyl)acrylate (3b)

FT-IR (KBr, cm<sup>-1</sup>): 3479, 2993, 2231, 1714, 1633, 1608, 1245. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.60 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.37–7.27 (m, 5H), 6.45 (s, 1H), 5.89 (s, 1H), 5.60 (s, 1H), 5.17 (s, 2H), 3.23 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  160.87, 148.72, 142.54, 131.66, 128.71, 127.59, 119.48, 113.92, 73.73, 53.83. Anal. Calc. for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>: C 73.72; H 5.11; N 4.77 %. Found: C 73.24; H 5.16; N 4.58 %.

## Benzyl 2-(hydroxy(4-(trifluoromethyl)phenyl)methyl) acrylate (3c)

FT-IR (KBr, cm<sup>-1</sup>): 3461, 2961, 1714, 1620, 1261. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.61 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.35-7.25 (m, 5H), 6.45 (s, 1H), 5.89 (s, 1H), 5.62 (s, 1H), 5.17 (s, 2H), 3.13 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  188.23, 171.76, 155.62, 141.52, 136.56, 129.60, 125.49, 123.28, 113.82, 72.63, 58.26. Anal. Calc. for C<sub>18</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>: C 64.29; H 4.46 %. Found: C 64.28; H 4.39 %.

### Benzyl 2-(hydroxy(3-nitrophenyl)methyl)acrylate (3d)

FT-IR (KBr, cm<sup>-1</sup>): 3489, 2961, 1714, 1631, 1531, 1351, 1265. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.25 (s, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.51 (t, 1H), 7.36–7.27 (m, 5H), 6.48 (s, 1H), 5.95 (s, 1H), 5.66 (s, 1H), 5.17 (s, 2H), 3.23 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  165.67, 148.32, 143.55, 141.00, 135.11, 132.65, 128.63, 128.52, 128.22, 127.53, 122.78, 121.60, 72.65, 67.00. Anal. Calc. for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>: C 65; H 4.79; N 4.47 %. Found: C 64.98; H 4.76; N 4.48 %.

### Benzyl 2-(hydroxy(2-nitrophenyl)methyl)acrylate (3e)

FT-IR (KBr, cm<sup>-1</sup>): 3437, 2964, 1715, 1634, 1610, 1528, 1350, 1247. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) & 7.95 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.65 (t, 1H), 7.44 (t, 1H), 7.35–7.10 (m, 5H), 6.45 (s, 1H), 6.22 (s, 1H), 5.80 (s, 1H), 5.22 (d, J = 12.1 Hz, 1H), 5.11 (d, J = 12.1 Hz, 1H), 3.43 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) & 165.71, 140.56, 136.12, 135.32, 133.55, 128.89, 128.74, 128.58, 128.34, 128.09, 126.93, 124.67, 67.77, 66.85. Anal. Calc. for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>: C 65; H 4.79; N 4.47 %. Found: C 64.99; H 4.79; N 4.48 %.

# Benzyl 2-((4-formylphenyl)(hydroxy)methyl)acrylate (3f)

FT-IR (KBr, cm<sup>-1</sup>): 3461, 2962, 17, 1632, 1608, 1262. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  10.00 (s, 1H), 7.85 (d, J = 8 Hz, 2H), 7.55 (d, J = 8 Hz, 2H), 7.34 (m, 3H), 7.27 (m, 2H), 6.44 (s, 1H), 5.89 (s, 1H), 5.64 (s, 1H), 5.16 (s, 2H), 3.1 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  165.719, 146.58, 141.05, 135.14, 132.24, 128.54, 128.23, 127.42, 127.25, 118.74, 111.55, 72.85, 66.96. Anal. Calc. for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>: C 72.97; H 5.40 %. Found: C 72.99; H 5.39 %.

### Benzyl 2-(hydroxy(phenyl)methyl)acrylate (3g)

FT-IR (KBr, cm<sup>-1</sup>): 3453, 2950, 1719, 1632, 1439. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.23-7.41 (m, 5H), 7.22-7.09 (m, 5H), 6.54 (s, 1H), 5.89 (s, 1H), 5.62 (s, 1H), 5.17 (s, 2H), 3.31 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  150.24, 140.15, 137.13, 132.13, 123.42, 119.21, 116.71, 114.21, 112.23, 109.13, 101.59, 55.22, 46.78. Anal. Calc. for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>: C 76.69; H 6.01 %. Found: C 76.61; H 6.04 %.

### Methyl 2-(hydroxy(4-nitrophenyl)methyl)acrylate (3h)

FT-IR (KBr, cm<sup>-1</sup>): 3423, 2960, 1718, 1609, 1525, 1348, 1263. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.30 (d, *J* = 8.1 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 2H), 6.76 (s, 1H), 5.78 (s, 1H), 5.90 (s, 1H), 3.98 (s, 3H), 3.13 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  188.23, 171.76, 155.62, 141.52, 136.56, 129.60, 125.49, 123.28, 113.82, 72.63, 58.26. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  173.13, 154.27, 150.21, 139.18, 130.14, 121.25, 120.34, 72.79, 49.14. Anal. Calc. for C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>: C 55.69; H 4.64; N 5.90 %. Found: C 55.68; H 4.61; N 5.89 %.

# Methyl 2-((4-cyanophenyl)(hydroxy)methyl)acrylate (3i)

FT-IR (KBr, cm<sup>-1</sup>): 3465, 2986, 2235, 1716, 1629, 1619, 1252. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.59 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.44 (s, 1H), 5.89 (s, 1H), 5.62 (s, 1H), 3.57 (s, 3H), 3.23 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  167.77, 146.62, 141.44, 130.23, 126.81, 125.39, 117.38, 111.82, 71.62, 50.63. Anal. Calc. for C<sub>12</sub>H<sub>11</sub>NO<sub>3</sub>: C 66.36; H 5.07; N 6.45 %. Found: C 66.34; H 5.11; N 6.46 %.

### Methyl 2-(hydroxy(3-nitrophenyl)methyl)acrylate (3j)

FT-IR (KBr, cm<sup>-1</sup>): 3479, 2959, 1717, 1630, 1528, 1341, 1258. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  8.27 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.54 (t, 1H),

Scheme 2 Synthesis of star-like polyionic Lewis base catalyst



6.43 (s, 1H), 5.92 (s, 1H), 5.65 (s, 1H), 3.76 (s, 3H), 3.31 (s, 1H).  $^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  172.14, 149.31, 142.28, 137.23, 131.18, 130.26, 122.71, 120.61, 119.52, 72.51, 49.32. Anal. Calc. for C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>: C 55.69; H 4.64; N, 5.90 %. Found: C 5567; H 4.48; N 5.91 %.

# Methyl 2-((4-formylphenyl)(hydroxy)methyl)acrylate (3k)

FT-IR (KBr, cm<sup>-1</sup>): 3436, 2963, 1744, 1705, 1630, 1608, 1247. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  10.02 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 6.39 (s, 1H), 5.87 (s, 1H), 5.63 (s, 1H), 5.65 (s, 1H), 3.76 (s, 3H), 3.24 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  175.23, 160.66, 142.42, 140.38, 131.28, 130.33, 119.23, 114.62, 71.51, 52.46. Anal. Calc. for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>: C 65.45; H 5.45 %. Found: C 65.47; H 5.45 %.

#### Methyl 2-(hydroxy(2-nitrophenyl)methyl)acrylate (3 l)

FT-IR (KBr, cm<sup>-1</sup>): 3433, 2965, 1719, 1631, 1609, 1530, 1375, 1261. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) & 7.93 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.59 (t, 1H), 7.48 (t, 1H), 6.49 (s, 1H), 6.28 (s, 1H), 5.83 (s, 1H), 3.72 (s, 3H), 3.14 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) & 163.32, 144.15, 143.13, 132.24, 127.32, 120.41, 117.13, 113.34, 63.42, 50.59. Anal. Calc. for C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>: C 55.69; H 4.64; N 5.90 %. Found: C 55.67; H 4.64; N 5.87 %.

### Methyl 2-(hydroxy(4-(trifluoromethyl)phenyl)methyl) acrylate (3m)

FT-IR (KBr, cm<sup>-1</sup>): 3465, 2958, 1718, 1616, 1259. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.71 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 6.45 (s, 1H), 5.77 (s, 1H), 5.69 (s, 1H), 5.36 (s, 1H), 3.60 (s, 3H), 3.14 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  187.29, 170.88, 156.74, 140.63, 136.47, 128.68, 114.76, 71.68, 56.46. Anal. Calc. for C<sub>12</sub>H<sub>11</sub>FO<sub>3</sub>: C 55.38; H 4.23 %. Found: C 55.34; H 4.28 %.

### **Results and discussion**

Star-like polyionic Lewis base catalyst 11 was prepared via several successive steps in acetonitrile in good yield (Scheme 2). At first, (3-chloropropyl)-trimethoxysilane was reacted with N, N N', N'-tetramethylethylenediamine at 80 °C for 3 days to afford the ionic liquid 6. Then, immobilization of ionic liquid 6 on freshly prepared nanosilica was carried out according to the literature [20] and led to the ionic liquid immobilized nanosilica 7. As shown in Scheme 2, increasing the length of the ionic chain of compound 7 was achieved via the four subsequent reactions with 1,4-dichlorobutane and N,N,N',N'-tetramethylethylenediamine to provide the Lewis base-tethered star-like polyionic nanocatalyst 11. The structure of the catalyst was confirmed by FT-IR spectrometry, FE-SEM, EDX and CHNS analysis.

6000

5000

4000

3000

2000

1000

0

nanosilica. b FE-SEM image of polyionic immobilized nanosilica. c FT-IR spectra of nanosilica and polyionic immobilized nanosilica



Fig. 2 a EDX analysis of ionic immobilized nanosilica 7. b EDX analysis of polyionic immobilized nanosilica 11

Immobilization was confirmed by FE-SEM image and FT-IR spectrometry of the product. Particle sizes in FE-SEM images of nanosilica and the ionic liquid-immobilized nanosilica were 30 and 60 nm, respectively (Fig. 1a, b). The signal at 1488  $\text{cm}^{-1}$  in the FT-IR spectrum of polyionic-immobilized nanosilica was related to the C-H bond and this signal was absent in the FT-IR spectrum of nanosilica (Fig. 1c). The existence of elements C, N, Si, Cl and

O in polyionic immobilized nanosilica was confirmed and analyzed by EDX and CHNS analysis (Fig. 2). Measuring of N:C ratio in compounds 7, 9 and 11 by CHNS analysis showed that this ratio was decreased by the growth of the polyionic chain. Immobilization of the polyionic compound on nanosilica was also confirmed by comparison of N:C ratio in two structures. Comparison of theoretical N:C ratio (0.259) with the elemental analyzed experimental

Table 1	Different	conditions	for the	synthesis	of	product	3g
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Entry	Solvent	Catalyst number	Reaction time (h)	Yield (%) <sup>a</sup>
1	CHCl <sub>3</sub>	6	7	15
2	$CH_2Cl_2$	6	7	10
3	CHCl <sub>3</sub>	7	7	20
4	$CH_2Cl_2$	7	7	15
5	CHCl <sub>3</sub>	9	7	29
6	$CH_2Cl_2$	9	7	26
7	CHCl <sub>3</sub>	11	7	38
8	$CH_2Cl_2$	11	7	40
9	CH <sub>3</sub> CN	7	7	35
10	CH <sub>3</sub> CN	9	7	52
11	CH <sub>3</sub> CN	11	7	55
12	[bmim]Cl	_	7	_
13	[bmim]Cl	6	7	_
14	[bmim]Cl	7	7	48
15	[bmim]Cl	9	7	65
16	[bmim]Cl	11	7	75

<sup>a</sup> Isolated yield

ratio (0.258) of product 7 also confirmed the structure of this compound. Also, comparison of theoretical N:C ratio (0.241) with the elemental analyzed experimental ratio (0.246) of immobilized catalyst 11 also confirmed the structure of this compound. As it was cleared from elemental analysis data, the N:C ratio was more decreased by growth of ionic chain [19].

We first carried out a model reaction involving benzaldehyde, benzyl acrylate and a Lewis base catalyst 7, 9 or 11 (Scheme 2) to optimize reaction conditions. As shown in Table 1, different conditions were examined for optimization of the model reaction. The reaction was examined in ionic liquid 6 as a reaction medium and Lewis base catalyst. On monitoring of the reaction by TLC, no significant progress in the reaction was observed after 7 h at 80 °C (Table 1; entry 13). This process was also examined in the presence of compounds 7, 9 or 11 as heterogeneous Lewis base nanocatalysts in acetonitrile at 80 °C. The yield obtained in the presence of these catalysts was much higher than it was in the absence of the catalyst. These reactions gave product 3g of 35, 52 and 60 %, respectively, after 7 h (based on benzaldehyde). This shows that the performance of catalyst 11 was better than catalysts 7 or 9. In addition, the length of ionic chain had a pronounced effect on the yield. The yield was not increased at higher temperatures and in other organic solvents (Table 1; entries 1-11). Excellent yields were obtained when employing catalyst 11 in [bmim]Cl as the reaction medium at room temperature. The model reaction proceeded smoothly to give a 75 % yield of 3g after 7 h under these conditions. By varying the amount of catalyst 11 with respect to benzaldehyde, we also obtained the optimum amount of catalyst. It was found that the yield of the product increased with the catalyst varying from 0.05 to 0.10 ratios. The yield was not increased when more amount of catalyst was employed.

Under the optimized reaction conditions, we examined the recovery of catalyst 11. When the reaction was completed, the catalyst was very simply recovered by washing all the soluble organic materials, reactants and products by ethyl acetate as eluent. The catalyst could be obtained with high recovery >90 % in each cycle. Meanwhile, high yield of 68–72 % of the model reaction could be obtained, mediated by the recovered catalyst within three cycles. It showed that catalyst 11 could be well recycled without remarkable loss of reaction activity.

The generality of this promising reaction was evaluated by employing a variety of benzaldehyde derivatives with (phenyl or methyl) acrylate. The corresponding results are shown in Table 2. As seen in Table 2, the reaction proceeded smoothly to afford the corresponding adducts in good to excellent yields for aromatic aldehydes bearing electron-withdrawing substituents. Benzaldehydes containing electron-donating groups, such as 4-OMe, 2-OMe and 4-Me did not react under optimized conditions. We examined this procedure on a 20 mmol scale and found that they underwent a smooth transformation to the related Baylis-Hillman adducts in good yields, suggesting that the present procedure is amenable to scale-up. The reaction of terephthalaldehyde with benzyl- and methyl acrylate was examined and found that only one aldehyde group of terephthalaldehyde reacted in this procedure. The products were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra and CHNS analysis. The comparison of their yields and reaction times with the reported value is shown in Table 3.

#### Conclusion

In summary, a kind of star-like polyionic Lewis base heterogeneous nanocatalyst could effectively accelerate the Baylis–Hillman reaction of aromatic aldehydes with (methyl or phenyl) acrylate. The catalyst could be easily recovered for reuse. Application of this catalyst for other reactions is under investigation and will be reported in due course.

Table 2Baylis–Hillmanreaction using star-like

	-
polyionic	nanocatalyst

Entry	$R_1$	R <sub>2</sub>	Product	Product number
1	CH <sub>2</sub> Ph	4-NO <sub>2</sub>	OH O OCH <sub>2</sub> Ph	3a
2	CH <sub>2</sub> Ph	4-CN	OH O OCH <sub>2</sub> Ph	3b
3	CH <sub>2</sub> Ph	4-CF <sub>3</sub>	NC <sup>C</sup> OH O OCH <sub>2</sub> Ph	3c
4	CH <sub>2</sub> Ph	3-NO <sub>2</sub>	F <sub>3</sub> C OH O O <sub>2</sub> N OCH <sub>2</sub> Ph	3d
5	CH <sub>2</sub> Ph	2-NO <sub>2</sub>	NO <sub>2</sub> OH O OCH <sub>2</sub> Ph	3e
6	CH <sub>2</sub> Ph	4-СНО	OH O OCH <sub>2</sub> Ph	3f
7	CH <sub>2</sub> Ph	Н	OH O OCH <sub>2</sub> Ph	3g
8	Me	4-NO <sub>2</sub>	OH O OCH3	3h
9	Me	4-CN	OH O OCH3	3i

#### Table 2 continued



Table 3 Comparison of the reactions times and yields with the reported values

Entry	Product number	Reaction time (h)		Yield (%) <sup>a</sup>	
		Found	Reported	Found	Reported
1	3a	5.5	10	96	93 [ <mark>20</mark> ]
2	3b	6	-	87	-
3	3c	6	-	89	-
4	3d	8	-	89	-
5	3e	6	-	90	-
6	3f	6.5	-	78	-
7	3 g	7	10	75	75 [ <mark>20</mark> ]
8	3 h	7	10	90	85 [ <mark>21</mark> ]
9	3i	7	12.5	88	88 [ <mark>21</mark> ]
10	3ј	8	11.5	87	84 [ <mark>21</mark> ]
11	3 k	8	-	72	-
12	31	7.5	24	85	79 [ <mark>22</mark> ]
13	3 m	7.5	-	83	-

<sup>a</sup> Isolated yield

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