# Supporting Information

## Layered double hydroxides anchored ionic liquids as amphiphilic heterogeneous catalyst for Knoevenagel condensation

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*Scaled-up synthesis of LDH-ILs-C12*

In a typical experiment, LDH-$NO_3$ (1.5 g) was added to formamide (500 mL) in a three necked flask, which was purged with $N_2$ to avoid carbonate contamination for 3h. Then the reaction mixture was under 60 kHz ultrasonication for 2 h. After that, the mixture was continuous vigorously stirred for 3 days under $N_2$ atmosphere. 13 mmol ILs-C12 was dissolved in $CH_3CN$ (25 mL) and added dropwise to the nanosheets suspension. The reaction mixture was stirred under $N_2$ for 24 h. 5 g $Na_2CO_3$ was dissolved in 10 ml $H_2O$ and added dropwise to the reaction mixture. After stirring for 1 h, the resultant precipitate of LDH-ILs-C12 was collected by centrifugation and washed with ethanol and water, and dried under vacuum overnight.

**Instruments**

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 infrared spectrometer by using KBr pellet method. The $^{1}H$-NMR and $^{13}C$-NMR spectra were recorded on a Bruker AV400 NMR spectrometer at resonance frequency of 400 MHz, and the chemical shifts were given relative to TMS as the internal reference. The solid-state $^{29}Si$ CP/MAS NMR experiment were record at 79.49 MHz with 60s pulse delay. The $^{13}C$ CP/MAS NMR were obtained at 100.62 MHz with 5s pulse delay. The $^{27}Al$ MAS NMR was carried out at 104.23 MHz with a 2s pulse delays. All the spectra were performed by using a Bruker Ascend Aeon 400 WB solid-state spectrometer equipped with a commercial 4 mm MAS NMR probe for $^{29}Si$ and $^{13}C$, and a commercial 2.5 mm MAS NMR probe for $^{27}Al$. The powder X-ray diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu-Kα radiation ($\lambda$ = 0.154 nm). Thermogravimetric (TG) analysis was performed on a STA-449C Jupiter (HCT-2 Corporation) at a heating rate of 10 $^{o}C$ $min^{-1}$ from 30 to 800 $^{o}C$ under $N_2$ (20 mL/min). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed on a Shimadzu ICPS-7500. BET measurements were performed at 77 K on a Quantachrome Autosorb-1C analyzer. $N_2$ adsorption-desorption isotherms were measured using a Quantachrome Autosorb-1 system at liquid nitrogen temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed using a monochromatized $Al_{K\alpha}$ exciting X-radiation (PHI

Quantera SXM). Contact angles were measured with a contact angle meter at 25 °C. Scanning electron microscopy (SEM) images were obtained using a Zeiss Supra 55 SEM. The basicity of the composites were probed by the temperature-programmed desorption of carbon dioxide ($CO_2$ TPD) using a PCA-1200 Chemical adsorption apparatus.

We use $CaCO_3$ as an internal standard substance for quantitative calculation of the basic sites of hydrotalcite samples. The samples (70 mg) and $CaCO_3$ (20 mg) were degassed by heating at 100℃ for 1 h under a He stream 30 mL $min^{-1}$ and then treated with $CO_2$ stream (30 mL $min^{-1}$) at 100℃ for 25 min. Physically adsorbed $CO_2$ was removed by a flushing He stream at 100℃ for 10 min. Chemisorbed $CO_2$ was desorbed by heating from about 30℃ up to 900℃ at a rate of 10 $^{o}C$ $min^{-1}$. The corresponding products were analysed by using an Agilent 7820A gas chromatography (GC) system using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 mm coating (HP-5). Yields were determined by GC analysis using reference standards. Assignments of the corresponding products were analysed by $^{1}H$ NMR and $^{13}C$ NMR spectroscopy.

**Table S1.** ICP-AES measurements of the composition of different samples.

| Materials | Mg[a] | Al[a] | N[a] | Formula |
|---|---|---|---|---|
| LDH-$CO_3$ | 18.18 | 6.05 | - | $Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.125}\cdot 0.5H_2O$ |
| LDH-ILs-C4 | 8.31 | 2.77 | 0.80 | $Mg_{0.75}Al_{0.25}[O_3SiC_{10}H_{20}N_2]_{0.036}[Br]_{0.036}(OH)_{1.92}[CO_3]_{0.175}\cdot 0.59H_2O$ |
| LDH-ILs-C8 | 8.08 | 2.70 | 0.75 | $Mg_{0.75}Al_{0.25}[O_3SiC_{14}H_{28}N_2]_{0.035}[Br]_{0.035}(OH)_{1.92}[CO_3]_{0.175}\cdot 0.64H_2O$ |
| LDH-ILs-C12 | 7.62 | 2.52 | 0.74 | $Mg_{0.75}Al_{0.25}[O_3SiC_{18}H_{36}N_2]_{0.036}[Br]_{0.036}(OH)_{1.92}[CO_3]_{0.175}\cdot 0.83H_2O$ |
| Reused LDH-ILs-C12 | 7.59 | 2.51 | 0.74 | $Mg_{0.75}Al_{0.25}[O_3SiC_{18}H_{36}N_2]_{0.036}[Br]_{0.036}(OH)_{1.92}[CO_3]_{0.175}\cdot 0.85H_2O$ |

[a] Analyzed by TCP-AES or elemental analysis; The formula was determined by TG-DTA, ICP-AES and elemental analysis.

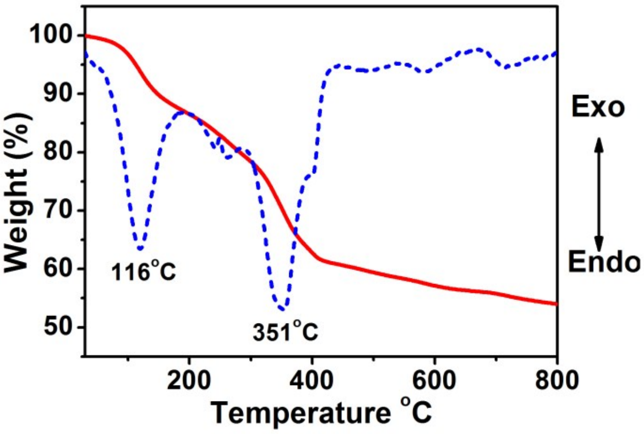


**Figure. S1** TG-DTA profile of LDHs-ILs-C4.

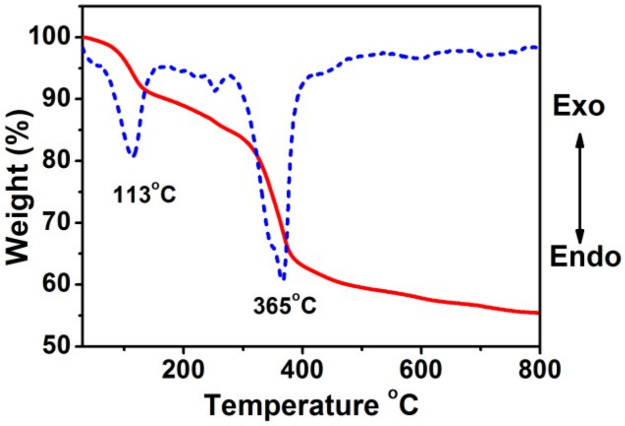


**Figure. S2** TG-DTA profile of LDHs-ILs-C8.

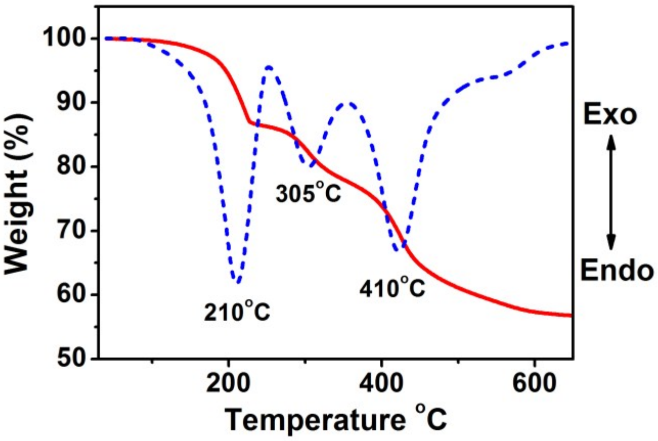


**Figure. S3** TG-DTA profile LDH-$CO_3$.

**Table S2.** Comparison of physicochemical properties LDH-ILs-Cn (n=4, 8, 12).

| Materials | Surface area[a] ($m^2 \cdot g^{-1}$) | Pore volume[b] ($cm^3 \cdot g^{-1}$) | Average pore size[c] (nm) |
|---|---|---|---|
| LDH-ILs-C4 | 25 | 0.05 | 3.5 |
| LDH-ILs-C8 | 25 | 0.05 | 4.2 |
| LDH-ILs-C12 | 28 | 0.06 | 4.8 |

[a] specific surface area calculated by the BET method in the relative adsorption pressure ($P/P_0$); [b] total pore volume determined by $N_2$ desorption at relative pressure; [c] average pore diameter obtained from the desorption isotherm by the BJH method.

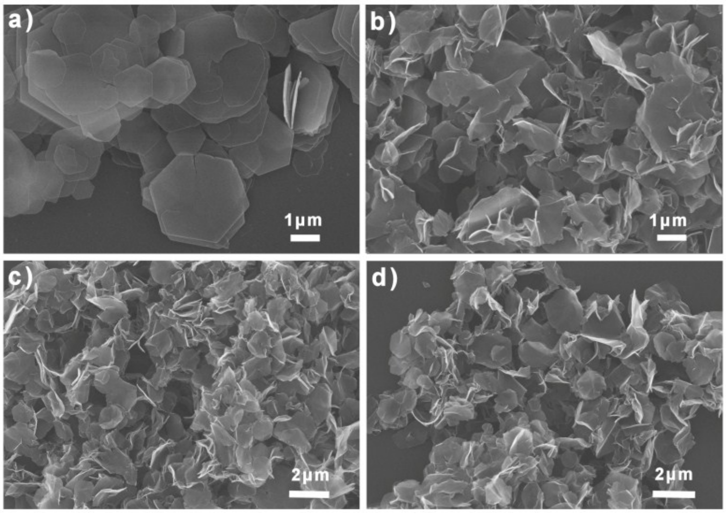


**Figure. S4** SEM images of a) LDH-$CO_3$, b) LDH-ILs-C4, c) LDH-ILs-C8, d) LDH-ILs-C12.

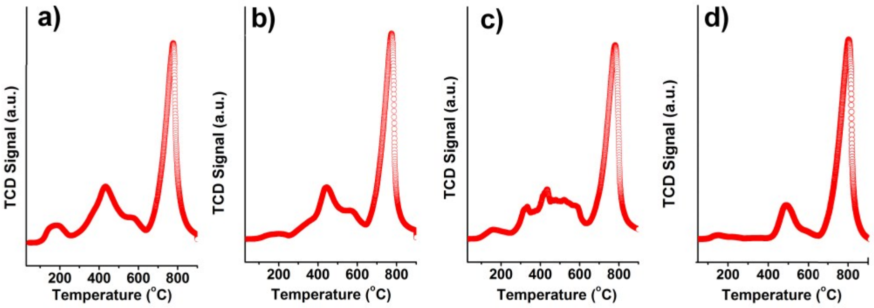


**Figure. S5**. The $CO_2$-TPD curves of a) LDH-ILs-C4, b) LDH-ILs-C8, c) LDH-ILs-C12 and d) LDHs-$CO_3$ with carbonate as the intercalated anions in the interlayer.

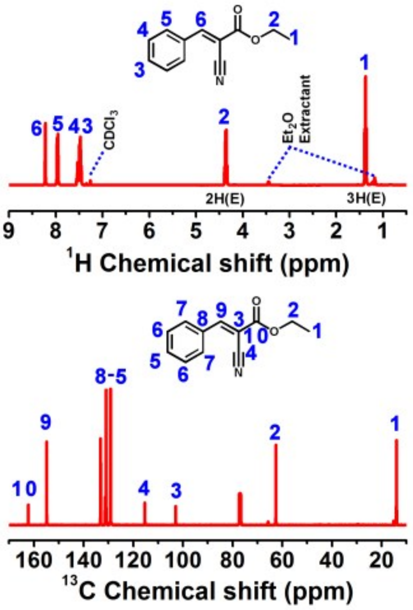


**Figure. S6** The $^1$H NMR and $^{13}$C NMR spectra of the product of Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

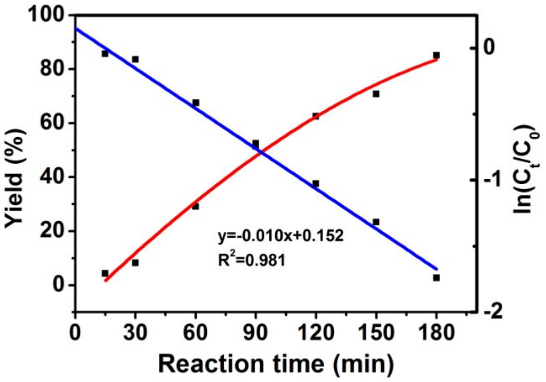


**Figure. S7** Kinetic profile of the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate catalyzed by LDH-ILs-C4 (red line: yield of corresponding products; red line: ln($C_t$/$C_0$), data were obtained by carrying out parallel experiments under the same experimental conditions).

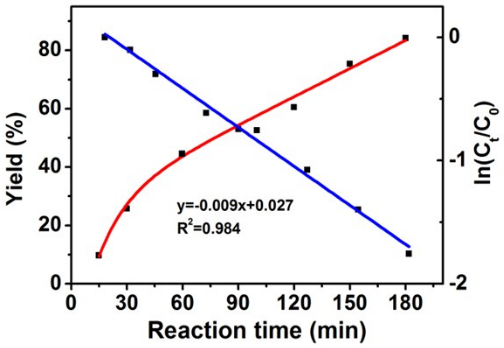
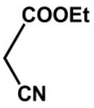
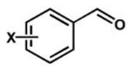
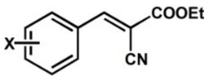
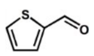
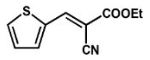
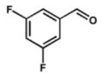
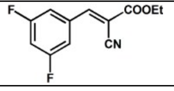
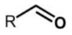
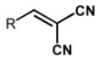


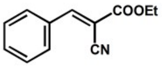
**Figure. S8** Kinetic profile of the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate catalyzed by LDH-ILs-C8 (red line: yield of corresponding products; red line: ln($C_t/C_0$), data were obtained by carrying out parallel experiments under the same experimental conditions).

**Table S3.** The Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate catalyzed by LDH-$CO_3$ at room temperature in aqueous solution.[a]

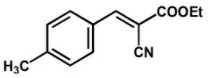
| Entry | Donor | Acceptor | Product | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| |  |  |  | | |
| 1 | | X=H | X=H | 3 | 19.0 |
| 2 | | X=2-Me | X=2-Me | 2 | 33.9 |
| 3 | | X=3-Me | X=3-Me | 2 | 13.9 |
| 4 | | X=4-Me | X=4-Me | 2 | 8.4 |
| 5 | | X=2-MeO | X=2-MeO | 2 | 32.5 |
| 6 | | X=3-MeO | X=3-MeO | 2 | 30.4 |
| 7 | | X=4-MeO | X=4-MeO | 2 | 8.6 |
| 8 | | X=2-Cl | X=2-Cl | 2 | 16.6 |
| 9 | | X=3-Cl | X=3-Cl | 2 | 19.4 |
| 10 | | X=2-Br | X=2-Br | 2 | 17.2 |
| 11 | | X=3-Br | X=3-Br | 2 | 21.1 |
| 12 | | X=4-Br | X=4-Br | 2 | 37.4 |
| 13 | | X=2-$NO_2$ | X=2-$NO_2$ | 2 | 57.3 |
| 14 | | X=3-$NO_2$ | X=3-$NO_2$ | 2 | 57.7 |
| 15 | | X=4-$NO_2$ | X=4-$NO_2$ | 2 | 63.0 |
| 16 | |  |  | 2 | 21.0 |
| 17 | |  |  | 2 | 17.1 |
| | |  |  | | |
| 18 | | R=$C_7H_{15}$ | R=$C_7H_{15}$ | 2 | 18.6 |
| 19 | | R=$C_9H_{19}$ | R=$C_9H_{19}$ | 2 | 6.1 |
| 20 | | R=$C_{10}H_{21}$ | R=$C_{10}H_{21}$ | 2 | 7.6 |

[a]Reaction conditions: 1 mmol Substrate, 1.5 mmol ethyl cyanoacetate, 30 mg catalyst LDH-$CO_3$, 0.5 mL $H_2O$, rt. [b]Yields were determined by GC analysis using reference standards. Assignments of corresponding products were analyzed by $^1$H NMR and $^{13}$C NMR spectroscopy.

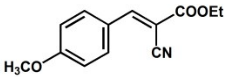
## $^1$H and $^{13}$C data of resulting products



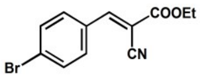
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.23 (s, 1H), 7.91 (d, 2H), 7.45-7.56 (d, 3H), 4.37 (m, 2H), 1.37 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.3, 154.9, 133.2, 131.3, 130.9, 129.1, 115.4, 102.9, 62.6, 14.2.



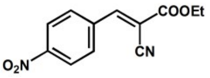
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.19 (s, 1H), 7.59 (d, 2H), 7.40 (d, 2H), 4.33 (m, 2H), 2.40 (m, 3H), 1.31 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.1, 154.6, 137.6, 130.1, 128.9, 128.5, 129.1, 102.7, 60.9, 21.3, 14.2.



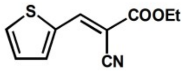
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.23 (s, 1H), 8.00 (d, 2H), 7.16 (d, 2H), 4.33 (m, 2H), 3.81 (m, 3H), 1.27 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.1, 159.8, 154.6, 130.2, 124.4, 117.5, 115.4, 102.9, 60.9, 55.8, 14.2.



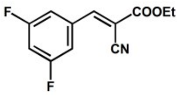
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.20 (s, 1H), 7.78 (d, 2H), 7.60 (d, 2H), , 4.33 (m, 2H), 1.31 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.2, 154.6, 133.3, 131.5, 131.0, 122.9, 102.9, 60.9, 14.2.



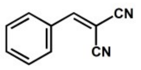
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.37 (d, 2H), 8.30 (m, 1H), 8.03 (d, 2H), 4.33 (m, 2H), 1.27 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.1, 154.6, 147.1, 138.2, 131.5, 123.8, 102.7, 60.9, 14.2.



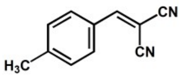
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.61(s, 1H), 8.09 (d, 1H), 7.74 (d, 1H), 7.33 (t, 2H), 4.30 (m, 3H), 1.27 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.1, 157.0, 137.8, 130..5, 129.1, 128.3, 117.5, 93.5, 60.5, 14.2.



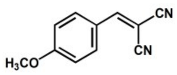
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.18 (s, 1H), 6.73 (s, 2H), 6.56 (s, 1H), 4.33 (m, 2H), 1.29 (t, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 162.1, 160.5, 137.6, 154.5, 138.4, 109.5, 103.9, 102.7, 60.5, 14.2.



$^{1}$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 7.79 (s, 1H), 7.58(d, 2H), 7.39(d, 2H), 7.33 (d, 1H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 161.5, 131.2, 128.6, 128.4, 127.9, 113.6, 81.4.



$^{1}$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 7.83 (s, 1H), 7.60 (d, 2H), 7.39(d, 2H), 2.41 (m, 3H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 161.5, 137.5, 128.9, 128.4, 128.2, 113.6, 81.2, 21.3.



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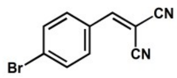
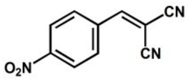
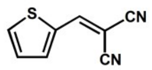


$^{1}$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 7.79 (s, 1H), 7.61(d, 2H), 7.76(d, 2H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 161.5, 131.5, 130.4, 128.5, 122.3, 113.6, 81.4.



$^{1}$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 8.37 (d, 2H), 8.00(d, 2H), 7.93(s, 1H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 161.5, 147.2, 137.5, 129.0, 123.3, 113.6, 81.4.



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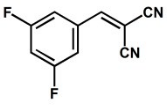

$^{1}$H-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 7.79 (s, 1H), 6.73(s, 2H), 6.56(s, 1H); $^{13}$C-NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ= 161.5, 159.8, 138.4, 113.6, 110.0, 103.9, 81.3.