Heterogenization of homogeneous chiral polymers in metal–organic frameworks with enhanced catalytic performance for asymmetric catalysis†

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Metal–organic framework (MOF)-based asymmetric heterogeneous catalysts have attracted increasing attention; however, some challenges need to be addressed, such as the rigidity of chiral auxiliary groups within MOFs and the lack of a versatile methodology for the facile construction of chiral MOFs. To address this issue, in this study, a mechanistically distinct approach was developed for heterogenizing linear chiral catalysts in the MOF cavities, rather than the synthetic modification of MOFs. This strategy involves the facile in situ polymerization of pre-impregnated chiral monomers within MOFs, affording the hybrid composites featuring a locally homogeneous and globally heterogeneous structure. The introduced chiral catalytic sites would be flexible in the pores, offering an opportunity to exploit its cooperative effect with the nearby catalytic metal nodes. The advantages of the chiral polymer/MOF composites were clarified by their excellent diastereoselectivity and recycling capacity for catalyzing the asymmetric Aldol reaction, which were superior to those of individually heterogeneous and homogeneous catalysts.

Introduction

Biological systems often seamlessly integrate multiple, cooperative functionalities to facilitate specific, highly selective chemical transformations, which have been typically revolutionary in artificial catalytic systems, especially for reusable heterogeneous catalysts. Nevertheless, some challenges still remain for the design and synthesis of multifunctional heterogeneous catalysts comprising cooperative active sites related to the spatial separation of the active sites within the rigid framework.

As a green and sustainable technology, metal–organic frameworks (MOFs) have been rapidly emerging as an extremely powerful platform for asymmetric catalysts. Kim, Lin, Duan, Cui, and other research groups have successfully reported that a series of homochiral MOFs exhibit catalytic activities for various asymmetric transformations. Generally, the strategies reported for the synthesis of homochiral MOFs are categorized into two groups: (1) direct assembly of compatible chiral organic bridging ligands and metal clusters and (2) introduction of chiral auxiliary groups into the organic linker or unsaturated metal node of achiral MOFs by post-synthetic modifications. With such strategies, all of these introduced catalytic centers were tightly fixed to the wall or metal nodes of MOFs with individual compartments separated by a distance, which would limit the cooperative effect between different catalytic sites within MOFs. Thus far, the studies related to the mimicking of biological systems by multi-functionalizing chiral MOFs with cooperative effects are extremely rare. Besides, the nature of a complete heterogeneous catalyst renders it difficult to exactly expose its catalytic sites to substrates in organic reactions because of its limited dissolution in the heterogeneous state. Hence, it is of particular importance to develop an attractive alternative functionalization approach for synthesizing chiral MOFs as a green and efficient biomimetic system with the potential for integrating multiple, cooperative functionalities.

To address these challenges, in this study, a mechanistically distinct approach was developed for heterogenizing linear chiral catalysts in the MOF cavities. This strategy was inspired by recent studies of MOF/polymer composites reported by Kitagawa’s group, in which MOFs can accommodate func-
Results and discussion

Cr-MIL-101 and L-proline were selected as a pair of cooperative catalysts

Previously, several studies have demonstrated that the combination of Lewis acids and L-proline as the co-catalyst afforded reaction products, with a significantly improved yield and enantioselectivity.\textsuperscript{53,54} Thus, in our study, Cr-MIL-101 was selected as the host material because of its large apparent surface area and uniformly distributed Lewis acid sites,\textsuperscript{55,56} and L-proline was used as a model chiral catalyst.\textsuperscript{57,58} Indeed, the addition of Cr-MIL-101 as the co-catalyst, which does not exhibit any catalytic activity (Fig. S1†), can remarkably improve the catalytic performance of L-proline with 75% yield, 86% ee, and 4:1 dr, while only an extremely low yield (20%) and poor diastereoselectivity (1.1:1) were achieved using 5 mol% of L-proline as the homogeneous catalyst (Fig. S1†).

In situ polymerization of chiral monomers impregnated within Cr-MIL-101

The preparation of the chiral polymer/MOF composites MIL-101-PP1 is accomplished in two steps via an in situ polymerization strategy: (1) a solution of the L-proline-containing vinyl derivative S1 (L-proline-containing vinyl monomer, see the ESI for the details), methyl acrylate and 2,2-azobisobutyronitrile (AIBN) in toluene is impregnated into the porous cavities of Cr-MIL-101; (2) following the incorporation of the monomers, the in situ radical copolymerization of the preloaded vinyl compounds was carried out within the MOF framework, affording the polymer/MOF composites MIL-101-PP1-Boc. The subsequent deprotection of N-Boc groups afforded the desired composite MIL-101-PP1. Fig. 2 shows the topological characteristics of Cr-MIL-101, the vinyl monomer, and the linear chiral polymer PP-1. Their compatible molecular sizes facilitated the complete penetration of the impregnated monomer fluids through the nano-space inside Cr-MIL-101. In addition, the amount of the added monomer solution was not greater than the pore volume of Cr-MIL-101; thereby most of them were left in the pores. An adequate contact time was required to ensure a thermodynamic equilibrium for the monomer penetration. Next, the monomers were polymerized through windows connecting the different cages of Cr-MIL-101 and intertwined together.

After polymerization, chiral polymeric chains were immobilized within the ordered mesopores of Cr-MIL-101, as shown...
in Fig. 1; the l-proline moieties were adequately intertwined with the MOF architecture by a sufficient number of methyl acrylate groups as copolymerization units. Due to the nature of linear, relatively short, and isolated polymeric chains within the MOF, the dissolution/swelling process of l-proline-containing polymers would be facile because of the minimized polymer–polymer interaction. The dissolution of the chiral polymeric chains PP1, which were extracted from MIL-101-PP1, is significantly easier than that of the typically used l-proline-containing cross-linked CPP1 resin (see the ESI for details, Fig. S2†). For a catalyst to be of interest, all catalytic sites within the composites should be sufficiently exposed to the reaction substrates in such a locally homogeneous domain. Besides, the completely solvated polymers can be spatially trapped within the MOF framework, and the leaching of the polymers would not be allowed during catalysis. The facile separation of the composites from the reaction mixtures can be achieved, resulting in their green/sustainable features. Thus, the structures of the synthesized MOF/chiral polymer composites are considerably different from those of homochiral MOFs12–28 and the conventional functionalized cross-linked polyethylene resins,59 both of which are pure heterogeneous materials.

Morphological characterization of MIL-101-PP1

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images revealed the predominant polymerization of vinyl monomers inside the Cr-MIL-101 mesopores without the bulk polymer on the external surface (Fig. 3b and Fig. S3†). In addition, the powder X-ray diffraction (PXRD) patterns of both composites were similar to that of Cr-MIL-101, confirming the retention of the parent framework structure with octahedron-like morphology. The intensity decreased in the small angle range (2θ, 5–7°), which generally corresponded to the local electron density distortion of the MIL-101 crystal structure upon pore filling (Fig. 4d). The gas
adsorption behaviours of these MOFs (Fig. 3d) revealed that the chiral polymer/MOF composites MIL-101-PP1 still exhibit high porosity (BET surface area of MIL-101-PP1: 531.2 m² g⁻¹). Neat Cr-MIL-101 exhibited a type-I N₂ isotherm with stepwise N₂ uptake in the range of 0.1–0.2 p/p°, while PP1 encapsulated within Cr-MIL-101 exhibited a relatively smooth N₂ isotherm, indicative of a higher amount of a heterogeneous internal surface because of the incorporated polymer. The calculated Brunauer–Emmett–Teller (BET) surface area decreased from 2980.2 m² g⁻¹ (pore volume = 1.81 mL g⁻¹) for Cr-MIL-101 to 531.2 m² g⁻¹ (pore volume = 0.33 mL g⁻¹) for MIL-101-PP1. Such a drastic decrease in the surface area is related to the mass fraction increase of Cr-MIL-101 and immobilized polymers; thus, the introduced PP1 must be present inside the cavities of Cr-MIL-101. Nevertheless, the pore volume (0.33 mL g⁻¹) of MIL-101-PP1 would still provide sufficient guest-accessible room for catalysis.

Characterization of internal polymers intertwined into Cr-MIL-101

The linear polymer PP1 intertwined into the MIL-101-PP1 cavities was released and collected by the digestion of Cr-MIL-101 under basic conditions (see the ESI† for details). The released polymers were characterized by ¹H NMR spectroscopy (Fig. 3a). Overall, the proton chemical shifts and integral area were consistent with those of PP1, which was prepared under homogeneous conditions without Cr-MIL-101 (see the ESI† for details). More specifically, the broad peaks ranging from 4 to 4.5 ppm corresponded to the heteroatom-attaching aliphatic H of L-proline and benzyl hydrogen protons, while the broad peaks between 6.5 and 7.4 ppm corresponded to the aromatic H of L-proline, demonstrating the successful anchorage of L-proline during in situ copolymerization. Meanwhile, the FTIR spectra of MIL-101-PP1 revealed two new peaks at ~3000 and ~1220 cm⁻¹ and ~1700 cm⁻¹, corresponding to the alkyl and carbonyl groups of L-proline/methyl acrylate, respectively (Fig. 3c); these peaks were also observed in the spectra of PP1 prepared under homogeneous conditions without Cr-MIL-101 (see the ESI† for details). Thus, the comparison of the FTIR spectrum of neat Cr-MIL-101 provides additional evidence for the immobilization of L-proline and polymerization of the alkyl moiety into the cavities of Cr-MIL-101. Moreover, according to the proton spectral analysis of the released polymer PP1 with the addition of an internal standard (i.e., trimesic acid),
the molar ratio of the l-proline moiety attaching the polymers to trimesic acid can be calculated by the comparison of the integral areas of the characteristic peaks of 4-benzoxly-l-proline (broad peak, δ ranging from 6.5 to 7.4 ppm) and trimesic acid (single peak, δ 8.37 ppm), affording the catalyst loading amount (related to the proline amount in the material) of the prepared composites MIL-101-PP1 (eqn (1)). Next, the in situ polymerization of impregnated chiral monomers within Cr-MIL-101 was extensively carried out to investigate the effect of the amount of methyl acrylate (copolymeric vinyl monomers, 5, 10, and 20 equiv.) in in situ polymerization; to our delight, the promising catalyst loading amount (l-proline moiety loading, 0.28 mmol per g of the composites, Table 1) was achieved using a 1:5 molar ratio of the l-proline-containing vinyl derivative S1 to methyl acrylate (5 equiv.) for polymerization. With the dilution of the concentration of catalytic sites, the catalyst loading amount (l-proline moiety) dramatically decreased, i.e., 0.05 mmol l-proline moiety per gram of the composites (methyl acrylate, 10 equiv.) and <0.01 mmol l-proline moiety per gram of the composites (methyl acrylate, 20 equiv.) (Table S1, characterization can be seen in Fig. S4, Table S2†). This dramatic decrease in the loading amount is related to the remarkably increased flexibility of the linear polymers with an additional decrease in the loading amount is related to the remarkably increased flexibility of the linear polymers with an additional decrease in the loading amount (related to the proline amount in the conventional l-proline-containing cross-linked polystyrene resin CPPI (BET surface: 17.9 cm2 g−1; pore volume: 0.015 mL g−1, see the ESI† for details) afforded the desired product in 33% yield with poor diastereoselectivity (3:1 dr) and enantioselectivity (41% ee).

Furthermore, the catalytic ability of the simple physical mixture of Cr-MIL-101/CPPI and Cr-MIL-101/PP1 for the Aldol reaction was not as good as that of MIL-101-PP1, only affording the desired product with yields of 35% (5.6:1 dr, 84% ee) and 64% (4.5:1 dr, 76% ee). By relating the catalytic ability from these contrasting experiments to their structural characteristics and the results from other l-proline-bearing homochiral MOF catalysts (i.e., CMIL-1,13 Cd-TBT;20 Zn-MOF1,21 Ap@3,23 Al-MIL-101-NH-Gly-Pro,28 IRMOF-Pro,62 DUT-32-NHPro,63 and UiO-68-NHPro,64 Fig. 4a), the synergistic effect of high porosity and Lewis acidity of Cr-MIL-101 is thought to be beneficial to the catalytic ability of l-proline in the asymmetric Aldol reaction, which would be attributed to more opportunity to have a cooperative effect between linear polymers threading within MOFs and their nearby catalytic metal nodes (Fig. 4b). Besides, the importance of metal clusters was demonstrated by a control experiment; we blocked the chromium sites of MIL-101-PP1 with pyridine coordination13,65 and found that the catalytic ability of pyridine-grafted MIL-101-PP1 for the Aldol reaction was significantly decreased, only affording the desired product 3a in 42% yield (3.1:1 dr, 58% ee).

Then, the filtration experiment was performed; a suspension of p-nitrobenzaldehyde (0.1 mmol), cyclohexanone (0.1 mL) and MIL-101-PP1 (5 mol%, related to the proline amount in the material) was stirred for 4 hours, and then, MIL-101-PP1 was filtered off and the filtrate was stirred for another 20 hours. We found that the conversion of the reaction was stopped in the absence of MIL-101-PP1, with only 52% yield. We also analyzed the catalyst loading amount of the recovered MIL-101-PP1 from the catalysis (run once); the active sites (related to the proline amount in the material, 0.23 mmol per g of the composites, Table S2†) in the composites can be

### Table 1 Textural structure and amount of the active site of the catalytic composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (mL g⁻¹)</th>
<th>Amount of the active site (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-MIL-101</td>
<td>2980.2</td>
<td>1.81</td>
<td>0</td>
</tr>
<tr>
<td>MIL-101-PP1</td>
<td>531.2</td>
<td>0.33</td>
<td>0.28a</td>
</tr>
<tr>
<td>PP1</td>
<td>—</td>
<td>—</td>
<td>1.41a</td>
</tr>
<tr>
<td>CPPI</td>
<td>17.9</td>
<td>0.015</td>
<td>1.55b</td>
</tr>
</tbody>
</table>

*a Active site is defined as l-proline groups on the polymer and the amount is determined based on the loadings of the polymer in the composites (eqn (1)). b The amount is determined based on elemental analysis.

Catalytic performance of MIL-101-PP1 in a symmetric Aldol reaction

After the chiral polymer/MOF composites were prepared, they were applied as heterogeneous catalysts in the asymmetric direct Aldol reaction. To our delight, MIL-101-PP1 with a loading of 5 mol% (related to the proline amount in the material) efficiently catalyzed this reaction, affording 3a in 91% yield with excellent diastereoselectivity (anti: syn = 12:1) and enantioselectivity (92% ee) (Fig. 4a), with turn-over frequency (TOF) and turn-over number (TON) values of 0.76 h⁻¹ and 18.2, respectively. Furthermore, we found that there is no further elimination by-product (crotonization reaction) in our catalysis, by comparing with a control compound (Fig. S7†).

In contrast, an extremely low yield (20%) and poor diastereoselectivity (1.1:1) were achieved using 5 mol% of l-proline as the homogeneous catalyst under otherwise identical reaction conditions. Besides, the use of 5 mol% (related to the proline amount in the material) of the conventional l-proline-containing DUT-32-NHPro63 and UiO-68-NHPro64, Fig. 4a), the synergistic effect of high porosity and Lewis acidity of Cr-MIL-101 is thought to be beneficial to the catalytic ability of l-proline in the asymmetric Aldol reaction, which would be attributed to more opportunity to have a cooperative effect between linear polymers threading within MOFs and their nearby catalytic metal nodes (Fig. 4b). Besides, the importance of metal clusters was demonstrated by a control experiment; we blocked the chromium sites of MIL-101-PP1 with pyridine coordination13,65 and found that the catalytic ability of pyridine-grafted MIL-101-PP1 for the Aldol reaction was significantly decreased, only affording the desired product 3a in 42% yield (3.1:1 dr, 58% ee).
maintained. Therefore, the compact intertwining state of linear chiral polymers and the MOF architecture renders them as robust heterogeneous materials. Furthermore, with the aim to demonstrate the greenness and sustainable profile of MIL-101-PP1, it was isolated and reused; the yield of the 5th run was about 91% of the value of the 1st run (Fig. 4c).

Furthermore, compared with the PXRD peaks of MIL-101-PP1 and MIL-101-PP1 (recycled) (Fig. 4d), the peak patterns of both the composites were similar, confirming the retention of the parent framework structure with octahedron-like morphology. The slight widening of the peaks and the weakened intensity of low angle peaks (5°–9°) can also be observed in the PXRD of MIL-101-PP1, since the recycled MIL-101-PP1 becomes much thinner during the reaction.

These preliminary results encouraged us to explore the generality of the reaction system by using various aldehydes. A series of aromatic aldehydes bearing electron-withdrawing groups at different positions of the phenyl ring efficiently reacted, affording the expected products 3b–3g in good-to-excellent yields (63–99%, Table 2) with excellent enantioselectivities for the major isomer (87–96% ee) and good-to-excellent diastereoselectivity (8:1 to >20:1 dr) (entries 1–6). Next, bulk aldehyde 1h was examined (entry 7), the size of which is even greater than the window size of Cr-MIL-101. However, the desired product was only obtained in trace amount using 5 mol% MIL-101-PP1 as the catalyst even after 5 days (in contrast, the product was obtained in 81% yield using 20 mol% of l-proline as the catalyst for 24 h under homogeneous conditions), demonstrating that catalysis mainly occurs within the MOF pores; hence, reagent size selectivity is verified for such a heterogeneous catalyst.

**Conclusion**

In this study, highly porous chiral polymer/MOF composites were prepared by a rational design, featuring a strategy involving the *in situ* polymerization of pre-impregnated chiral monomers within MOFs. The chiral catalytic sites attached within the linear polymers were flexible; hence, a synergetic effect between the chiral catalytic sites and Lewis acidic metal nodes is observed for the catalysts. Moreover, the presence of locally homogeneous domains within the globally heterogeneous host rendered benefits of both homogeneous and heterogeneous characteristics to this catalytic system. As expected, excellent diastereo- and enantioselectivites were observed for the asymmetric direct aldol reaction compared with those observed for heterogeneous and homogeneous catalysis. Therefore, our strategy opens a new perspective for the development of chiral MOFs and other materials as artificial, green and efficient biomimetic systems readily and economically. Currently, studies aimed at extending this strategy to other linear polymers and various applications (e.g., asymmetric catalysis, chromatography, and sensing) are underway in our laboratory.

**Experimental section**

**Chemicals and characterization**

NMR spectra were recorded on a Bruker DPX-400/500 spectrometer at 400/500 MHz for $^1$H NMR and 100/125 MHz for $^{13}$C NMR. The data for $^3$H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. The data for $^{13}$C NMR are reported in terms of chemical shift (δ, ppm). Mass spectra were recorded on an Esquire-LC-0075 mass spectrometer. All infrared experiments were performed on a Bruker Alpha FT-IR spectrometer using 1 mg of the solid sample at 4 cm$^{-1}$ resolution. Powder X-ray diffraction (PXRD) data were obtained at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα ($\lambda = 1.5418$ Å), with a scan speed of 1° per step and a 2θ range of 5°–40°. The Brunauer–Emmett–Teller (BET) surface areas were measured by using a Micromeritics ASAP 2020 analyzer at 77 K. Thermogravimetric analysis (TGA) data were obtained using a PerkinElmer TGA 7 system running from 50°C to 500°C with a scan rate of 10°C min$^{-1}$. The analyses of the morphology and chemical composition of the samples were conducted by using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). The computational modeling for the topological characteristics of the host, monomers, and linear polymers was achieved by using the Discovery Studio 2.5 program. Gel permeation chromatography (GPC) analysis was performed on a Waters 1525 system with a refractive index (RI) detector. The starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, and others).

**Table 2 MIL-101-PP1-catalyzed asymmetric Aldol reaction**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Time</th>
<th>Yield (%)</th>
<th>ee (%)</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b: R = m-NO$_2$</td>
<td>3b</td>
<td>36 h</td>
<td>86</td>
<td>92 (11:1)</td>
</tr>
<tr>
<td>1</td>
<td>1c: R = o-NO$_2$</td>
<td>3c</td>
<td>5 d</td>
<td>87</td>
<td>93 (13:1)</td>
</tr>
<tr>
<td>1</td>
<td>1d: R = p-Cl</td>
<td>3d</td>
<td>6 d</td>
<td>63</td>
<td>87 (8:1)</td>
</tr>
<tr>
<td>1</td>
<td>1e: R = p-CF$_3$</td>
<td>3e</td>
<td>24 h</td>
<td>70</td>
<td>93 (&gt;20:1)</td>
</tr>
<tr>
<td>1</td>
<td>1f: R = p-CN</td>
<td>3f</td>
<td>48 h</td>
<td>99</td>
<td>91 (8:1)</td>
</tr>
<tr>
<td>1</td>
<td>1g: R = pent-F</td>
<td>3g</td>
<td>24 h</td>
<td>89</td>
<td>96 (&gt;20:1)</td>
</tr>
<tr>
<td>1</td>
<td>1h: R = m-NO$_2$</td>
<td>3h</td>
<td>5 d</td>
<td>Trace</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*a* Reactions were carried out under neat conditions using 0.1 mmol aldehyde and 0.1 mL of ketone. *b* The yield was determined by $^1$H NMR spectroscopy of the crude reaction mixtures using dibromo methane as an internal standard. *c* The ee values were determined by chiral HPLC. *d* dr values (anti:syn) were determined by the $^1$H NMR analysis of the crude reaction mixtures; n.d. = not determined.
The synthesis of MIL-101-PP1 composites

A solution of compound S1 (300 mg, 0.86 mmol), methyl acrylate (4.3 mmol, as a co-polymeric monomer) and 2,2-azobisisobutyronitrile (AIBN, 42.3 mg, 0.26 mmol, as a radical initiator) in toluene (2 mL) was impregnated into Cr-MIL-101 (1 g), and the mixture was allowed to stand under a nitrogen atmosphere at 4 °C for 12 hours to reach a distribution equilibrium of the monomers through the cavities of MIL-101. The polymerization was conducted under a nitrogen atmosphere at 80 °C for 5 days. Then, the obtained powder was soaked in DMF for 3 days to completely remove all unreacted monomer and loosely attached polymers between MIL-101 particles. DMF was then removed by washing with CH2Cl2. Finally, the desired polymer MIL-101-PP1 was obtained by further de-protection of the N-Boc group in a mixture of CH2Cl2 (4 mL) and CF3CO2H (1 mL) for 4 hours at room temperature, and was successively washed with CH2Cl2 and dried at 80 °C overnight.

The extraction of linear polymers PP1 from MIL-101-PP1 composites

Prior to the deprotection of N-Boc, the MIL-101-PP1 composites (200 mg) were fully digested using 10 wt% sodium hydroxide aqueous solution (0.8 mL); then the mixture was acidified to neutral pH (pH ~ 7) using 6N hydrochloric acid. With the aim to precipitate terephthalic acid and salts (e.g. NaCl and CrCl3), acetone (50 mL) was added, and a brownish solution was obtained by filtration. Then, the extracted mixture was concentrated under vacuum to afford PP1-Boc. Subsequently, PP1-Boc was added to CH2Cl2 (4 mL) and CF3CO2H (1 mL) and stirred for 4 hours at room temperature to completely remove the N-Boc group, and the desired linear polymers PP1 were obtained by the evaporation of the reaction solvent.

Qualification for the L-proline loading amount with a unit of mmol g−1 in the MIL-101-PP1 composite

The MIL-101-PP1 composite (200 mg) was first fully digested with a mixture of 10 wt% NaOD and MeOH-d4 (1:2, v/v). The filtrate was collected and the internal standard trimesic acid (21 mg, 0.1 mmol) was added (slightly heated to dissolve it); then the 1H-NMR analysis of the mixture was performed. The molecular constitution of the released PP1 involves an L-proline-containing unit and methyl acrylate units; indeed, NMR analysis can exactly give the value of the PP1/trimesic acid molar ratio, which can be calculated by the ratio of the integral areas between the characteristic phenyl peaks of 4-benzyloxy-L-proline (lAPP1, broad peak, δ, ranging from 6.5 to 7.4 ppm) and trimesic acid (lAtimesic acid, δ, 8.37 ppm). Therefore, the L-proline loading amount with a unit of mmol g−1 can be calculated based on eqn (1):

\[
\text{lAPP1} = \frac{0.1 \times 3}{4} \times \frac{\text{WPP1}}{\text{WPP1}} \times 1000 \times \frac{200}{115}
\]

Typical reaction procedure for the Aldol reaction

A suspension of the aldehyde (0.1 mmol) and cyclohexanone (0.1 mL) and the corresponding chiral catalyst (0.005 mmol, 17.8 mg for MIL-101-PP1) was stirred at room temperature for the indicated time (Table 2). The reaction was quenched by adding ethyl acetate. Upon filtration, the catalyst was washed with CH2Cl2. The organic layers were collected and concentrated under vacuum. The crude product was checked by 1H NMR spectroscopy to obtain the reaction yield and diastereoselectivity (dr values) using dibromomethane as an internal standard, and was then purified by chromatography (petroleum ether/ethyl acetate) to afford the desired product. The ee value was determined by chiral stationary phase HPLC analysis.

Conflicts of interest

There are no conflicts to declare.

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