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Chiral Squaramide-Functionalized Imidazolium-Based Organic−Inorganic Hybrid Silica Promotes Asymmetric Michael Addition of 1,3-Dicarbonyls to Nitroalkenes in Brine

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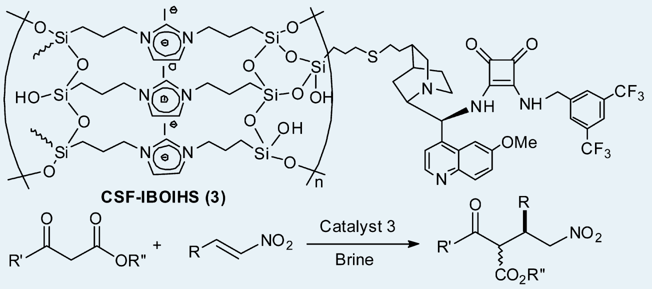
Supporting Information



ABSTRACT: Chiral cinchona-based squaramide-functionalized organic−inorganic hybrid silica is developed through postgrafting 3-mercaptopropyltrimethoxylsilane onto imidazolium-based organic−inorganic hybrid silica, followed by the anchor of a squaramide organocatalyst via a thiolene click method. Structural characterizations and spectroscopic analyses demonstrate that a well-defined single-site chiral cinchona-based squaramide active center is incorporated onto the organic−inorganic hybrid silica. As a bifunctional heterogeneous catalyst, it displays excellent catalytic activity and high enantioselectivity in asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes in brine. As presented in this study, the synergistic effect of confined site-isolated squaramide species and a salient imidazolium phase-transfer function significantly accelerates the catalytic performance. Furthermore, the organic−inorganic hybrid silica is conveniently recovered and reused at least eight times without loss of catalytic activity, showing an attractive feature in practice of organic transformation in an environmentally friendly manner.

KEYWORDS: *asymmetric catalysis, bifunctional catalysis, heterogeneous catalyst, imidazolium, organic−inorganic hybrid composites*

■ INTRODUCTION

As a type of environmentally friendly material, functionalized ionic liquids as supports for catalysis seen much success.[1] Among these ionic liquid-based heterogeneous catalysts, imidazolium-based organic−inorganic hybrid silica (IBOIHS)[2] shows superiority in heterogeneous catalysis. In addition to its general advantages, such as innocuity and nonflammability, IBOIHS can be prepared at large scale, which benefits potential applications in industry. Furthermore, imidazolium-based silane can be assembled easily through various self-assembly strategies, which opens up a broad range of opportunities to construct a variety of functionalized imidazolium-based heterogeneous catalysts.[2c−f] More importantly, the phase transfer function of the imidazolium functionality within the material can efficiently facilitate a catalytic reaction in a diphase catalytic system, which greatly promotes organic transformation in an aqueous medium. In addition, high thermal and chemical stability enables its convenient recovery, which provides a high recyclability. On the basis of these significant benefits, development of functionalized IBOIHS material for environmentally friendly catalysis is of considerable importance, which is still rare in the field of heterogeneous asymmetric catalysis.

Chiral cinchonine-based squaramides,[3] as one kind of important organocatalysts[4] for carbon−carbon bond formation reactions, have been investigated extensively in various asymmetric reactions. In particular, cinchona-based squaramide organocatalysts have exhibited excellent enantioselectivity in asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes.[5] Furthermore, some cinchonine-substituted squaramides can significantly accelerate asymmetric Michael addition in a brine reaction system, which is on the verge of being applied in industry.[5a,b] However, because of complicated preparation processes and the expensive price of chiral cinchona-based squaramides, recycling of these ligands is highly desirable. Although some works have investigated their recovery and recycling, most of them still suffer from low catalytic activity and enantioselectivity relative to their homogeneous counterparts.[6] Thus, exploration of a practical strategy and realization of highly efficient asymmetric Michael addition are still a scientific and technological challenge.

We are interested in heterogeneous asymmetric catalysis, especially in an effort to develop highly efficient silica-based heterogeneous catalysts.[7] Recently, we have found that an organic−inorganic hybrid silica within an imidazolium functionality within its silicate network efficiently facilitates an asymmetric transfer hydrogenation in an aqueous medium, whose imidazolium functionality acting as a phase transfer catalyst greatly enhances organic transformation.[7a,b] In this contribution, taking advantage of the imidazolium phase-transfer function, we conveniently incorporate chiral cincho-

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nine-substituted squaramide organocatalyst onto imidazolium-based organic−inorganic hybrid silica and construct a bifunctional heterogeneous catalyst. As presented in this study, this catalyst displays excellent catalytic activity and enantioselectivity in asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes in brine. It is also found that the synergistic effect of the imidazolium phase-transfer function and confined site-isolated squaramide species significantly promotes the catalytic performance. Furthermore, the functionalized organic−inorganic hybrid silica can be readily recycled and reused repeatedly at least eight times without obviously reducing its catalytic performance, making it an attractive catalyst in the practice of organic transformation in an environmentally friendly manner.

■ EXERIMENTAL SECTION

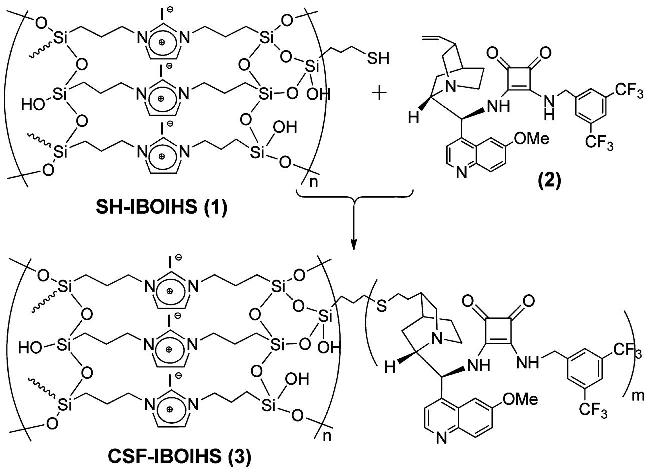
Preparation of the Catalyst 3. In a typical synthesis, a dry 50 mL round-bottom flask was charged with SH-IBOIHS (**1**) (0.10 g), squaramide (**2**) (16.10 mg, 0.025 mmol), and 2.0 mol % of 2,2-dimethoxy-1,2-diphenylethanone photoinitiator, backfilled with argon, and irradiated for 27 h with a 15 W blacklight (λ_{max} = 365 nm). The resulting solid was filtered through filter paper and rinsed with excess methanol and dichloromethane. After Soxhlet extraction in dichloromethane solvent for 12 h to remove any homogeneous and unreacted starting materials, the solid was dried overnight at 60 °C under vacuum to afford heterogeneous catalyst (**3**) (0.11 g) as a light yellow powder. IR (KBr) cm^{-1}: 3434.6 (s), 3148.5 (w), 3093.8 (w), 2937.3 (w), 2882.4 (w), 1693.5 (m), 1629.2 (w), 1564.9 (m), 1454.1 (w), 1352.7 (w), 1196.2 (s), 1131.9 (s), 1039.8 (s), 920.5 (m), 717.8 (w), 643.9 (w), 487.5 (w), 431.7 (w). ^{29}Si MAS NMR (79.5 MHz): T^1 (δ = −51.7 ppm), T^2 (δ = −60.4 ppm), T^3 (δ = −69.5 ppm). ^{13}C CP MAS NMR (161.9 MHz): 184.7−181.1 ($\underline{C}$=O), 161.9−168.9 ($\mathrm{CO\underline{C}\mathit{H}{=}\underline{C}HCO}$), 155.9, 146.8, 143.3−117.5 ($\underline{C}$ of Ar, Ph and CF$_3$), 136.7, 123.5 ($\underline{C}$H of of imidazolium), 62.3 ($\mathrm{N\underline{C}HCH_2Ar}$), 56.9 ($\mathrm{O\text{-}\underline{C}H_3}$), 55.7−46.7 ($\mathrm{SiCH_2CH_2\underline{C}H_2N}$ and $\underline{C}$ connected to N atom without connected to arometic ring), 43.7 ($\mathrm{N\text{-}\underline{C}H_2Ar}$), 40.1 ($\mathrm{\underline{C}C_2}$), 30.6 ($\mathrm{\underline{C}H_2}$ group connected to S atom), 30.7−19.2 ($\mathrm{SiCH_2\underline{C}H_2CH_2N}$, $\underline{C}$ of cyclic alkyl groups in cycling group without connected to N atom and other acyclic alkyl groups), 10.1 ($\mathrm{Si\underline{C}H_2CH_2CH_2N}$ and $\mathrm{Si\underline{C}H_2}$) ppm. Elemental analysis (%): C, 29.15; H, 6.19; N, 7.08; S, 0.65.

General Procedure for Asymmetric Michael Addition of 1,3-Dicarbonyls to Nitroalkenes. A typical procedure was as follows: Catalyst **3** (68.50 mg, 5.0 μmol of squaramide based on TG analysis), nitrostyrene (1.0 mmol), 1,3-dicarbonyl (2.0 mmol), and 5.0 mL of brine were added to a 10 mL round−bottom flask in turn. The mixture was allowed to react at 25 °C for 20−60 min. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the heterogeneous catalyst was filtered through filter paper for the recycle experiment. The aqueous solution was extracted by Et$_2$O (3 × 3.0 mL). The combined Et$_2$O was washed with brine twice and dehydrated with Na$_2$SO$_4$. After the evaporation of Et$_2$O, the residue was purified by silica gel flash column chromatography to afford the desired product. The conversion was calculated by the internal standard method, and the ee value could be determined by chiral HPLC analysis with a UV−vis detector using a Daicel OD-H, AS-H, or AD-H chiralcel column (Φ 0.46 × 25 cm). The absolute configurations of compounds were assigned by comparison of their optical rotations to the literature values.

■ RESULTS AND DISCUSSION

Synthesis and Structural Characterization of the Heterogeneous Catalyst. Chiral squaramide-functionalized imidazolium-based organic−inorganic hybrid silica, abbreviated as CSF-IBOIHS (**3**), was prepared as outlined in Scheme 1.

Scheme 1. Preparation of the Heterogeneous Catalyst 3



First, the imidazolium-based organic−inorganic hybrid silica was synthesized through the hydrolysis−condensation of disilylated 1,3-bis(3-(triethoxysilyl)propyl)-1*H*-imidazol-3-ium iodide[8] according to the reported procedure.[2a] The direct postgrafting of 3-mercaptopropyltrimethoxylsilane onto IBOIHS did then afford mercapto-functionalized SH-IBOIHS (**1**) in the form of a white powder. Finally, the heterogeneous catalyst **3** was obtained successfully via a thiolene click reaction[9] of SH-IBOIHS (**1**) and chiral squaramide (**2**) (see the Experimental Section and Figures S1−S3 of the Supporting Information (SI)). The thermal gravimetric (TG) analysis revealed that the loadings of chiral cinchonine-based squaramide in catalyst **3** was 47.50 mg (0.073 mmol) per gram of catalyst (see Figure S2 in the SI).

Incorporation of chiral squaramide within the imidazolium-based organic−inorganic hybrid silica could be confirmed by the solid-state ^{13}C cross-polarization (CP) MAS NMR spectrum. As shown in Figure 1, catalyst **3** produced the

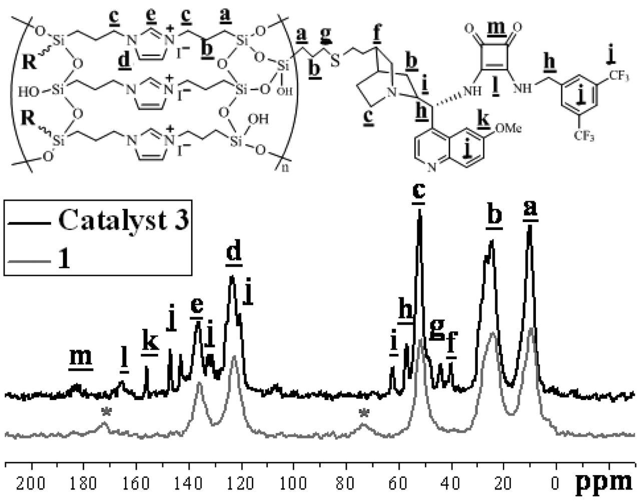


Figure 1. Solid-state ^{13}C MAS NMR spectrum of catalyst **3**.

strong carbon signals of $Si\underline{C}H_2\underline{C}H_2\underline{C}H_2N$ groups at 10.1, 24.6, and 52.6 ppm, corresponding to a propyl-bridged moiety. The characteristic carbon signals at 123.4 and 136.7 ppm were ascribed to the carbon atoms of the imidazolyl moiety. All these carbon signals were the same as those of its parent IBOIHS.[2a] In addition, the weak carbon signals of the carbonyl groups, the aromatic rings, and the alkyl groups in the chiral cinchona-based squaramide moiety that were marked in its spectrum could be clearly observed. These peaks were absent in the spectrum of SH-IBOIHS (**1**), suggesting that the chiral cinchona-based squaramide had been grafted onto SH-IBOIHS (**1**). These chemical shifts of weak carbon signals in catalyst **3** are similar to those of its homogeneous counterpart,[5b,c] demonstrating that catalyst **3** had the same well-defined single-site active species as its homogeneous squaramide organocatalyst.

The organosilicate network and composition of chiral cinchona-based squaramide onto the imidazolium-based organic–inorganic hybrid silica could be further confirmed by the solid-state ^{29}Si MAS NMR spectra. As shown in Figure 2, both SH-IBOIHS (**1**) and catalyst **3** produced one group of exclusive T signals that were derived from organosilica, suggesting that all Si species were covalently attached to carbon atoms. Typical isomer shift values of catalyst **3** are similar to those reported in the literature[10] (−48.5, −58.5, and −67.5 ppm for T^1, T^2, and T^3 {$[R(HO)_2SiOSi]$, $[R(HO)Si(OSi)_2]$, and $[RSi(OSi)_3]$}, respectively). The strongly characteristic signals of T series at −60.4 and −69.5 ppm corresponding to T^2 $[R-Si(OAr)_2(OH)]$ and T^3 $[R-Si(OAr)_3]$ (R = chiral cinchona-based squaramide moieties or propyl groups) in catalyst **3** demonstrated that catalyst **3** possessed an organosilicate network with $R-Si(OSi)_2(OH)$ and $R-Si(OSi)_3$ species as its main organosilicate network. In addition, the absence of signals for Q series from −90 to −120 ppm indicated that the carbon–silicon bond was not cleaved during the hydrolysis–condensation process.

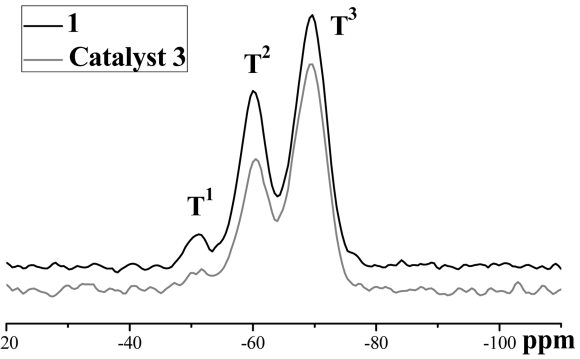


Figure 2. Solid-state ^{29}Si MAS NMR spectra of **1** and catalyst **3**.

The mesostructural morphology of catalyst **3** was further investigated using a nitrogen adsorption–desorption technique and scanning electron microscopy (SEM). As a result of the sharp adsorption step at high relative pressure values (0.78–0.98) with a very narrow H1 hysteresis loop (Figure 3),[11] a nitrogen adsorption–desorption isotherm disclosed that catalyst **3** was mesoporous and was composed of micrometer particles. The SEM image further confirmed its nanostructure, which is similar to that attained with the IBOIHS material[7a,b] (see Figure S3 in the SI). On the basis of the above studies, the imidazolium-based organic–inorganic hybrid silica with well-defined single-site cinchona-based squaramide active species could be readily obtained.

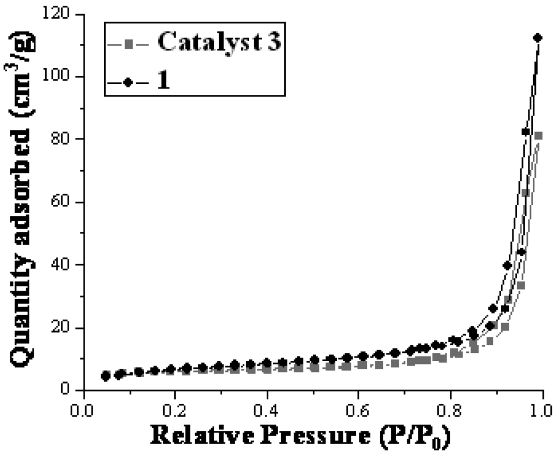
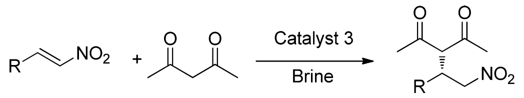


Figure 3. Nitrogen adsorption–desorption isotherms of **1** and catalyst **3**.

Catalytic Property of the Heterogeneous Catalyst. The asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes as one kind of important carbon–carbon bond formation reactions has been investigated extensively.[3,5,6] As presented in this study, we first examined the catalytic activity and enantioselectivity in asymmetric Michael addition of acetylacetone to nitrostyrene in brine solvent according to the reported method.[5a] As shown in entry 1 of Table 1, the catalytic reaction of acetylacetone and nitrostyrene gave (*S*)-3-(2-nitro-1-phenylethyl)pentane-2,4-dione with more than 99%

Table 1. Asymmetric Michael Addition of Acetylacetone to Nitroalkenes[a]



entry	R	time	conv (%)[b]	ee (%)[b]
1	Ph	20	>99 (98)	99 (99)[c]
2	Ph	60	93	97[d]
3	Ph	20	98	98[e]
4	Ph	120	98	99[f]
5	4-FPh	40	>99	99
6	4-ClPh	30	>99	99
7	4-BrPh	30	>99	99
8	4-MePh	30	>99	99
9	4-OMePh	30	>99	98
10	2-ClPh	60	>99	97
11	2,4-diClPh	40	>99	99
12	2-thienyl	20	>99	99
13	ethyl	20	>99	98
14	*i*-propyl	20	>99	99
15	*t*-butyl	20	>99	98

[a]Reaction conditions: catalyst **3** (68.50 mg, 5.0 μmol of squaramide based on TG analysis), nitroalkenes (1.0 mmol), acetylacetone (2.0 mmol), 5.0 mL of brine, reaction time 20–60 min. [b]Determined by chiral HPLC analysis (see Table S1 and Figure S4 in the SI). [c]Data were obtained using homogeneous squaramide as a catalyst. [d]Data were obtained at a substrate-to-catalyst mole ratio of 400. [e]Data were obtained using the mixed **1** plus **2**. [f]Data were obtained using a parallel SiO_2-based nanoparticle as a catalyst.

conversion and 99% ee value, which was comparable to that of its homogeneous cinchona-based squaramide organocatalyst[5a] (entry 1 versus 1 in the bracket). Furthermore, the asymmetric Michael addition of acetylacetone to nitrostyrene could be run at a very high ratio of substrate to catalyst without markedly affecting its ee value, as exemplified by the asymmetric reaction at a substrate-to-catalyst mole ratio of 400 (entry 2).

On the basis of the above excellent catalytic performance, the heterogeneous catalyst **3** was further investigated systemically in asymmetric Michael addition of acetylacetone to nitroalkenes in brine. As shown in Table 1, excellent conversions, no side products, and high enantioselectivities were obtained for all tested substrates under the same conditions. Moreover, the structures and electronic properties of substituents at the Ar moiety did not significantly affect their enantioselectivities, in which various electron-withdrawing and -donating substituents at the Ar moiety were equally efficient in this asymmetric Michael addition (entries 5−12).

To gain better insight into the heterogeneous catalysis and to eliminate the disturbance coming from residual homogeneous chiral cinchona-based squaramide (**2**) remaining via noncovalent physical adsorption onto the material, one controlling experiment for asymmetric Michael addition of acetylacetone to nitrostyrene was carried out using the mixed SH-IBOIHS (**1**) and homogeneous squaramide (**2**) as a catalyst under the same conditions. The result showed that the asymmetric reaction catalyzed by the above mixed catalyst did still afford the corresponding products with nearly the same conversion and ee value as its homogeneous counterpart (entry 3 in Table 1). This observation demonstrated that residual homogeneous chiral squaramide (**2**) remaining via noncovalent physical adsorption onto material also resulted in a catalytic performance, suggesting the presence of the homogeneous disturbance coming from noncovalent physical adsorption. However, when the above catalyst was treated with a thorough process of Soxhlet extraction, the reused catalyst gave only tiny amounts of the products. This observation disclosed that residual homogeneous squaramide remaining via noncovalent physical adsorption on catalyst **3** had been eliminated because catalyst **3** had passed through a stricter Soxhlet extraction during preparation. This fact eliminates the role of the homogeneous catalyst remaining via noncovalent adsorption and reveals that the nature of heterogeneous catalysis is indeed derived from the heterogeneous catalyst itself.

It is noteworthy that the catalytic reactions could be completed within a relatively short reaction time (between 20 and 60 min), which is rare in a generally heterogeneous catalysis system because common heterogeneous catalysts often have a slow reaction ratio in a heterogeneous reaction system. The phenomenon indicated that the imidazolium functionality in catalyst **3** may play an important role in promoting its catalytic performance. To prove the role of imidazolium functionality in catalyst **3**, we prepared a parallel chiral squaramide-functionalized SiO_2-based heterogeneous catalyst (nanoparticle) through a similar thiolene click reaction of SH-SiO_2 and chiral squaramide (**2**) (see the Experimental Section and Figure S3 in the SI). The only difference from catalyst **3** is that the above parallel nanoparticle has no imidazolium functionality within its inorganosilicate network. In this case, we compared its catalytic performance with catalyst **3**. The result showed that the catalytic reaction of acetylacetone and nitrostyrene catalyzed by the above parallel nanoparticle needed 2.0 h to complete the asymmetric transformation (entry 4). Notably, the obvious longer reaction time than that obtained with catalyst **3** (2.0 h versus 20 min) demonstrated the low catalytic efficiency because of the lack of imidazolium phase-transfer function in this parallel heterogeneous catalyst. In other words, a high reaction ratio in catalyst **3** should be due to the fact that the phase-transfer function of the imidazolium functionality within the organic−inorganic hybrid silica significantly promoted its catalytic performance. This behavior was also observed in imidazolium-based organic−inorganic hybrid silica materials in our previous reports.[7f−h] Further evidence to support this view came from a kinetic investigation shown in Figure 4. In this case, a comparison of the asymmetric reaction of acetylacetone and nitrostyrene catalyzed by catalyst **3** and the above parallel nanoparticle was performed. The results showed that the reaction catalyzed by catalyst **3** resulted in an initial activity higher than that achieved with the above parallel nanoparticle (the initial TOFs were 598.8 and 258.0 mol mol^{-1} h^{-1}, respectively). This investigation further confirmed that the enhanced reaction rate in the asymmetric reaction is attributed to the phase-transfer function of imidazolium functionality.

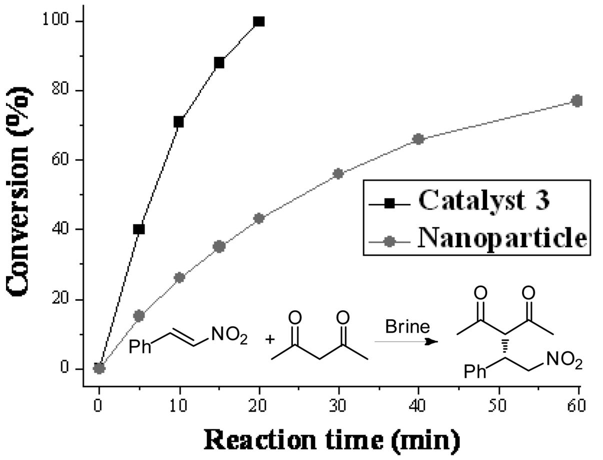
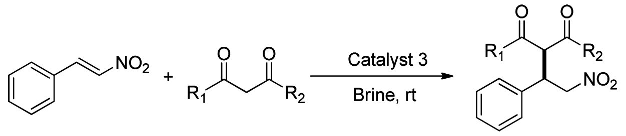
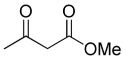
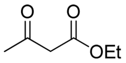
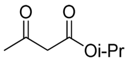
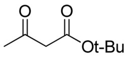
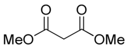


Figure 4. Comparison of the asymmetric Michael addition of acetylacetone to nitrostyrene catalyzed by catalyst **3** and its parallel catalyst. Reactions were carried out at 25 °C at a substrate-to-catalyst mole ratio of 200 in 5.0 mL of brine.

In addition to asymmetric Michael addition of acetylacetone to nitroalkenes, described in Table 1, the heterogeneous catalyst **3** could also be applied to asymmetric Michael addition of *β*-ketoesters to nitrostyrene in brine.[5a] As shown in Table 2, again, excellent conversions and enantioselectivities were observed for the tested substrates. Taking the asymmetric Michael addition of methyl acetylacetate to nitrostyrene as an example, it was found that the asymmetric reaction gave chiral products with more than 99% conversion and 99% ee value, which was comparable to those of its homogeneous counterpart, **2**.[5a−c] It should be noted that the large substrates, such as *i*-propyl acetylacetate and *t*-butyl acetylacetate (entries 3−4 in Table 2), could also be reacted with nitrostyrene to afford the chiral products with excellent conversions and enantioselectivities within 20 min, indicating that the open microstructure of IBOIHS allows the easy access of substrates, resulting in a high catalytic efficiency. Evidence to support this judgment came from the construction of (*R*)-2-acetyl-2-(2-nitro-1-phenylethyl)cyclopentanone. As shown in Scheme 2, asymmetric Michael addition of 2-acetylcyclopentanone to nitro-

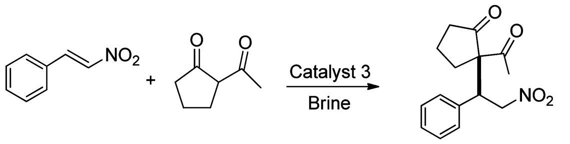
Table 2. Asymmetric Michael Addition of β-Ketoesters to Nitrostyrene[a]



Entry	Nucleophile	Time	Conv. (%)[b]	dr	Ee. (%)[b]
1		20 min	>99	1.2:1	99(99)
2		20 min	>99	1.3:1	99(98)
3		20 min	>99	1.6:1	98(98)
4		20 min	>99	1.8:1	98(97)
5		20 hour	90	/	94

[a]Reaction conditions: catalyst **3** (68.50 mg, 5.0 μmol of squaramide based on TG analysis), nitrostyrene (1.0 mmol), 1,3-dicarbonyls (2.0 mmol), 5.0 mL of brine. [b]Determined by chiral HPLC analysis (see Table S2 and Figure S5 in the SI).

Scheme 2. Asymmetric Michael Addition of 2-Acetylcyclopentanone to Nitrostyrene



99% conversion,
dr = 1.5:1, 99 (99)% ee

styrene afforded the corresponding chiral products with more than 99% ee value within 1.0 h. These results shown here suggested that the heterogeneous catalyst **3** can serve as a general heterogeneous catalyst promoting asymmetric Michael addition in brine.

An important feature of the design of the heterogeneous catalyst **3** was reliable separation via simple filtration, and the reused catalyst could still retain its catalytic activity and enantioselectivity through multiple cycles. As shown in Figure 5, the heterogeneous catalyst **3** had an obviously high reusability in asymmetric Michael addition of acetylacetone to nitrostyrene, in which the ee values as well as the conversions did not drop obviously after being recycled continuously eight times (see in Tabel S3 and Figure S6 in the SI).

In conclusion, taking advantage of the imidazolium phase-transfer function, we successfully immobilized a chiral cinchona-based squaramide organocatalyst onto imidazolium-functionalized organic−inorganic hybrid silica and report a bifunctional heterogeneous catalyst. The catalyst displays excellent catalytic activity and enantioselectivity in asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes in brine. As demonstrated in the present study, the excellent catalytic activity and high enantioselectivity are attributed to the synergistic effect of the imidazolium phase-transfer function and confined site-isolated cinchona-based squaramide organocatalyst. Furthermore, the heterogeneous catalyst was conveniently recovered and reused at least eight times without loss of the catalytic activity, which is attractive in the practice of organic transformation. This study described here also offers a general approach to immobilize various organocatalysts by significantly enhancing the asymmetric performance in an environmentally friendly and sustainable catalysis manner.

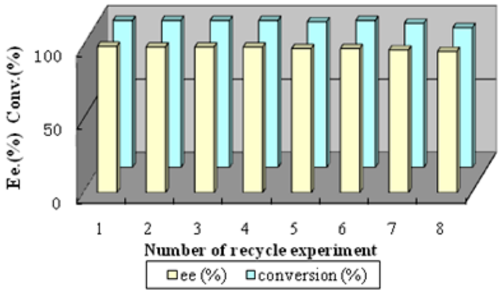


Figure 5. Reusability of catalyst **3** for asymmetric Michael addition of acetylacetone to nitrostyrene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization, and chiral HPLC analysis in the catalytic enantioselective reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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