Stabilization of α-ZrP ceramic nanosheets adsorbing quaternary ammonium ions in organic solvents and their application as a stable solid support for lipase catalyzing stereospecific synthetic reactions

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ABSTRACT
Herein, the effect of immobilizing lipase onto layered α-zirconium phosphate ceramic nanosheets (α-ZrP NS) on the enzymatic transesterification of allylic alcohols was investigated in organic solvents. α-ZrP NS modified with quaternary ammonium ions show a excellent dispersion stability in n-hexane. Lipase immobilized on α-ZrP NS enables the improved synthesis of chiral allylic alcohols and esters, with significantly reduced reaction times compared to reactions performed in the absence of α-ZrP NS. The coexistence of α-ZrP NS also results in more efficient steric inversion of the resulting alyl ester, suggesting the utility of α-ZrP NS as a support for lipase-induced stereospecific reactions. The present manuscript discusses on mechanisms of high dispersion stability of α-ZrP NS and their preferable immobilizing effect for the lipase inducing the steric inversion in detail.

1. Introduction
In general, enzymatic synthetic reactions provide high substrate and reaction route specificity. Moreover, they proceed under moderate reaction conditions such as atmospheric pressure, neutral pH, and moderate temperature [1]. To date, lipases that promote hydrolytic decomposition of lipids in living bodies have been frequently used for enzymatic asymmetric synthesis. Enzymes have also been applied toward the synthesis of various enantiopure compounds from racemic mixtures. For example, there have been so many reporting lipase-catalyzed resolutions from racemic mixture and diastereomeric mixtures via ester hydrolysis and transesterification reactions [1–15]. Needless to say, these enzymatic syntheses contribute to the progress of clean synthetic chemistry, which is highly desirable in modern chemical industry. Although lipases carry out regio- and stereoselective synthetic reactions at moderate temperatures, they show relatively low chemical durability and dispersibility in the solutions frequently used in synthetic chemistry (acids, bases, and organic solvents).

Chiral allylic alcohols and their derivatives are valuable substrates for many stereospecific allylic substitution reactions used to prepare versatile intermediates and artificial building blocks for pharmaceuticals, agrochemicals, and natural products [7–11]. For instance, the asymmetric Tsuji–Trost reaction and stereospecific allylation using chiral allylic alcohol derivatives are especially important strategies in synthetic organic chemistry [12–15]. However, these chiral allylic alcohol derivatives have been frequently prepared using complicated reaction systems and improvement and/or simplification of the reaction conditions are still an ongoing challenge, even in state-of-the-art organic syntheses.

Herein, we envisage that the kinetic resolution of racemic allylic alcohols via a lipase-catalyzed transesterification reaction may provide a more efficient and facile synthesis of chiral allylic alcohols and esters using lipase immobilized on layered α-zirconium phosphate nanosheets (α-ZrP NS) to enhance the dispersion stability of lipase in the reaction. In our previous study, the enhanced catalytic activity of lipase immobilized on titanate nanosheets (TNS) was demonstrated in the ester hydrolysis reaction [16]. In addition, Takagi and coworkers recently reported the enhanced catalytic activity of horseradish peroxidase (HRP) adsorbing on the synthetic clay nanosheets [17]. Even though this findings implied that inorganic nanosheets are potential candidates as a stable support for enzymes, the contribution of nanosheets was only observed in an aqueous solution [18]. The TNS precipitate in an organic solvent owing to their high surface energy based on small dimensions (<10 nm) and hydrophilic surface. Therefore, we attempted to replace TNS with α-zirconium phosphate nanosheets (α-ZrP NS) because the nanosheets with larger two-dimensional sizes (~10 μm) can be easily obtained through a simple
2. Experimental

2.1. Synthesis and exfoliation of layered α-zirconium phosphate (α-ZrP)

Layered zirconium phosphate (α-ZrP, Zr(HPO₄)₂) powder was synthesized using a conventional liquid phase reaction as follows: ZrOCl₂ octahydrate (10.0 g) was dissolved in H₂O (100 mL) followed by the addition of an aqueous solution of H₃PO₄ (85%, 11.83 mL). The resulting mixture was aged for 24 h at 90°C, and then cooled to room temperature. The resulting white precipitate was recovered via centrifugation (22,400 x g, 10 min, 20°C) and then repeatedly washed with H₂O until the unreacted chemical species were completely removed. The α-ZrP solid was dried for several hours under reduced pressure at 70°C to obtain white powder. According to the XRD measurement of the obtained powder, the pristine powder had monoclinic crystal structure with a space group of P2/c assigned to typical α-ZrP and its particle size distribution runs from 0.5 to 2 μm (Figure 1a).

The as-prepared α-ZrP powder was exfoliated in tetrahydrofuran (THF) or toluene containing tetrabutylammonium (TPA) hydroxide. The exfoliation of α-ZrP with quaternary ammonium hydroxides included two steps: (1) ion exchange of H⁺ in the interlayer space of α-ZrP with the bulky ammonium cations and (2) delamination of the monolayers due to the weakened electrostatic interactions between the host layers and the guest cations. During the exfoliation step, slightly wet α-ZrP powder had to be employed because complete dehydration (the extraction of coexistent H₂O molecules in the interlayer space) narrows the interlayer spacing of α-ZrP, making the insertion of ammonium cations more difficult. In the conventional exfoliation process of α-ZrP, tetrabutylammonium ions have been frequently employed to substitute H⁺ in the interlayer space of α-ZrP and to exfoliate laminated α-ZrP into Zr(PO₄)₂-x monolayers (α-ZrP NS, cation exchange capacity (CEC): 7.1 mmol/g). On the other hand, since the present study aims to utilize α-ZrP NS hybridized with lipase in several organic solvents, quaternary ammonium ions with longer alkyl chains are expected to be appropriate because the adsorption of such cations forms anionic α-ZrP NS with improved hydrophobicity. This would induce the enhanced dispersion stability of the hybrids in nonpolar solvents. Consequently, a solution of tetrabutylammonium hydroxide (TPAOH) was prepared via an anion-exchange method using tetrabutylammonium bromide. Tetrabutylammonium bromide (0.5 g) was dissolved in a mixed solvent composed of THF or toluene (2.53 mL) and absolute ethanol (0.5 mL), and an enough amount of highly basic anion-exchange resin with exchangeable hydroxide ions was then added to the solution. The mixture was stirred for 12 h at ambient temperature to complete the substitution of Br⁻ with OH⁻. The resulting solution containing the exfoliation reagent (1.4 mL) was added to α-ZrP powder (0.125 g) suspended in THF or toluene (0.25 mL) and the α-ZrP suspension was magnetically stirred for 24 h at ambient temperature to obtain a colloidal solution of the exfoliated α-ZrP NS (abbreviated below as ZrP (toluene) or ZrP (THF)). The concentration of α-ZrP NS in the colloid solutions, which was determined using inductor coupled plasma–atomic emission spectrometry (ICP-AES) after diluting the solution with a strong acid solution, was estimated to be [Zr] = 0.25 mM.

2.2. Synthesis of racemic allylic alcohols

Allylic alcohols (1a-d) as substrates of lipases were synthesized from their corresponding aldehydes using a traditional Grignard reaction. During the synthesis of racemic allylic alcohols and the transesterification of allylic alcohols using lipase in the presence or absence of α-ZrP NS mentioned the subsequent section, the procedures were performed under a nitrogen atmosphere in oven-dried glassware. All solvents and reagents were used as received unless stated otherwise. Analytical thin layer chromatography (TLC) was performed on precoated 0.25 mm thick silica gel 60-F₂₅₄ plates, visualized using UV light and KMnO₄ dip. NMR (¹H NMR at 400 MHz and ¹³C NMR at
Figure 1. (a) An SEM image of pristine α-ZrP powder, (b) photographs of n-hexane solutions containing α-ZrP NS exfoliated with TMA⁺ or TPA⁺, and (c) a particle size distribution curve of the colloidal solution of TPA⁺-α-ZrP NS.

100 MHz) spectra of products was recorded in a CDCl₃ solution containing tetramethylsilane (TMS) as an internal standard unless stated otherwise.

2.2.2. Rac-1-Phenylprop-2-en-1-ol (1a)
Vinylmagnesium chloride (2.1 M solution in THF, 28.6 mL, 60 mmol) was slowly added to a solution of benzaldehyde (3.25 g, 30 mmol) in THF (60 mL) at −78°C. The reaction mixture was stirred for several hours until the reaction was complete as-determined by TLC. The reaction mixture was allowed to warm to 0°C, and the reaction was quenched with a saturated aqueous solution of ammonium chloride (30 mL) and diluted with water (30 mL). After being warmed to room temperature, the reaction mixture was extracted with diethyl ether (20 mL). The aqueous layer was separated and extracted with diethyl ether (30 mL × 3). The combined organic layers were washed with brine (50 mL), dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude product was obtained as a yellow oil, which was purified using flash column chromatography on silica gel to give 1a (3.91 g, 73%) as a colorless oil.

2.2.2. Rac-2-Phenylbut-3-en-2-ol (1b)
Vinylmagnesium chloride (2.1 M solution in THF, 28.6 mL, 60 mmol) was slowly added to a solution of acetophenone (3.60 g, 30 mmol) in THF (60 mL) at −78°C. The reaction mixture was stirred for several hours until the reaction was complete as-determined by TLC. The reaction mixture was allowed to warm to 0°C, and the reaction was quenched with a saturated aqueous solution of ammonium chloride (30 mL) and then diluted with water (30 mL). After being warmed to room temperature, the reaction mixture was extracted with diethyl ether (20 mL). The aqueous layer was separated and extracted with diethyl ether (30 mL × 3). The combined organic layers were washed with brine (20 mL), dried over magnesium sulfate,
filtered, and concentrated in vacuo. The crude product was obtained as a yellow oil, which was purified using flash column chromatography on silica gel to give 1c (1.60 g, 97%) as a colorless oil.

2.2.4. Rac-1-(Pyridin-3-yl)prop-2-en-1-ol (1d)
Vinylmagnesium chloride (2.1 M solution in THF, 9.52 mL, 20 mmol) was added slowly to a solution of 3-pyridinecarbaldehyde (1.10 g, 10 mmol) in THF (20 mL) at 0°C. The reaction mixture was stirred for several hours until the reaction was complete as determined by TLC. The reaction was quenched with saturated aqueous solution of ammonium chloride (10 mL) and then diluted with water (10 mL). After being warmed to room temperature, the reaction mixture was extracted with diethyl ether (7 mL). The aqueous layer was separated and further extracted with diethyl ether (10 mL × 3). The combined organic layers were washed with brine (20 mL), dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude product was obtained as an orange oil, which was purified using flash column chromatography on silica gel to give 1d (0.76 g, 56%) as a yellow oil.

2.3. Lipase-ZrP catalyzed asymmetric transesterification of 1a-d
All reactions were carried out on a 2.0 mmol scale. Lipase (Lipase AK Amano, 50 mg, pl = 4.3, 20,000 U/g) and the α-ZrP NS colloidal solution (ZrP (toluene) or ZrP (THF), 0.25 mM, 0 ~ 30 μL) were suspended in n-hexane (5 mL). To study influence of the α-ZrP NS on the catalytic transesterification, comparative experiments were also carried out using an identical amount of pure THF or toluene instead without the ZrP(toluene) or ZrP(THF). The solution was stirred for 30 min at 40°C in order to combine lipase with the α-ZrP NS. Herein, lipase hybridized with and without α-ZrP NS are denoted as “lipase-ZrP” and “free lipase,” respectively. To confirm the adsorption of lipase to α-ZrP NS, the following experiment was performed. The α-ZrP NS and lipase modified with fluorescein isothiocyanate (FITC) in advance were mixed and stirred for several hours at room temperature. Then, the mixture was centrifuged for settling the hybrid particles composed of FITC-lipase and α-ZrP NS. Since the fluorescence intensity of supernatant (e.g. 495 nm, em: 530 nm) which is related to concentration of free (unbound) FITC-lipase was significantly reduced as compared with the original FITC-lipase solution, indicating the physical binding of lipase to α-ZrP NS in the present condition. Subsequently, allylic alcohol 1a (2.0 mmol) was added dropwise via a syringe. Furthermore, isopropenyl acetate (4.0 mmol) was added as an acyl donor and stirred for 16 h while monitoring the reaction process using TLC. After the reaction was completed, the reaction mixture was cooled to room temperature, filtered, and concentrated in vacuo. A mixture of chiral allylic alcohol 1a and ester 2a was obtained as pale yellow oil. Then, 1a and 2a were separated using flash column chromatography on silica gel (n-hexane/EtOAc = 95:5 ~ 80:20) to afford (S)-1a and (R)-2a in 44% and 45% yield, respectively. Enantiomeric excesses for allylic alcohol (S)-1a and ester (R)-2a were determined by chiral HPLC analyses, those absolute configurations were supposed based on retention times of allylic compounds for HPLC analysis. In the cases of 1b-d, the identical procedure was conducted. Spectral data (1H NMR, 13C NMR, and chiral HPLC) for the enantiomerically enriched allylic alcohols 1a-d and allylic acetates 2a-d are found in the Supplementary material.

3. Results and discussion
In general, inorganic ceramic nanosheets (NS) are commonly prepared by means of a top-down technique, that is, bulky layered crystals are exfoliated to nanosheets in the presence of exfoliating agents in an appropriate aqueous solution [21]. Moreover, the quaternary ammonium cations adsorb on surface of the exfoliated NS and then prevent aggregation of NS to form a stable colloidal solution. However, it is expected that inorganic nanosheets show poor dispersion stability in nonpolar solvents, which are frequently utilized for organic synthetic reactions, due to their hydrophilic surface. Therefore, the present study focused on a quaternary ammonium cation with longer alkyl chains as an exfoliation agent to increase in hydrophobicity and dispersion stability of α-ZrP NS in nonpolar solvents. If the strategy will succeed, α-ZrP NS play a role as stable supports for lipase with improved physicochemical properties. Consequently, we firstly investigated whether α-ZrP NS could be stabilized in a nonpolar solvent under the presence of tetraptentammonium (TPA+, longer) or tetramethylammonium (TMA+, shorter) ions.

The α-ZrP powder (0.5 g) was exfoliated in an absolute ethanol solution of tetramethylammonium (TMA) or tetraptentammonium (TPA) hydroxide (20 wt%, 10 mL). After stirring the suspension more than 2 days, unexfoliated α-ZrP was removed by centrifugation, and then the colorless and transparent colloidal solution was obtained. An aliquot of the obtained colloidal solutions (1.2 mL) was mixed with n-hexane (4 mL) that was a major part of a reactant medium during the transesterification denoted later. As shown in Figure 1(b), cotton-like white particles were observed in the solution including α-ZrP NS exfoliated with TMA+, suggesting aggregation of α-ZrP NS. In contrast, no discernible agglomeration was seen in the solution containing TPA+, implying stable dispersion of α-ZrP NS. In fact, optical absorption spectrum of the solution shows high transmittance over a wide
range of wavelength (\(\lambda = 300 \sim 800\) nm). These observations indicate that quaternary ammonium cations with longer alkyl chains are effective in highly dispersion of \(\alpha\)-ZrP NS in \(n\)-hexane as expected. These findings are not conflicted with the previous literature of which \(\alpha\)-ZrP NS modified with amphiphatic polyoxalkyleneamine are dispersible in toluene [22].

A particle size distribution curve of the stable colloidal solution estimated with a dynamic light scattering (DLS) method is displayed in Figure 1(c). A single broad peak is seen in the range of 400 \(\sim\) 1300 nm which may be concerned with the size distribution of the pristine powder (Figure 1(a)) and incomplete exfoliation process. These results imply that \(\alpha\)-ZrP NS are stabilized with TPA\(^+\) even in \(n\)-hexane although the \(\alpha\)-ZrP could not be delaminated to monolayers. Hence, it was demonstrated that the \(\alpha\)-ZrP NS exfoliated with TPA\(^+\) might be potential candidates as supports to improve enzymatic activity of lipase in nonpolar solvents for further investigations. [Figure 1 near here]

As revealed above, since TPA\(^+\)-modified \(\alpha\)-ZrP NS was dispersible in \(n\)-hexane, our interest subsequently focused on identifying the efficiency of lipase during the transesterification of several racemic alcohols according to Scheme 1. Initially, we investigated the difference in reactivity between secondary and tertiary allylic alcohols (1a and 1b) in the absence of \(\alpha\)-ZrP NS (Table 1, free lipase). A comparison of the reactivity against these alcohols showed that tertiary allylic alcohols (1b) were inactive in the lipase-catalyzed transesterification reaction. This may be due to steric hindrance around a reactive site of the allylic alcohol (C-OH). Hence, secondary allylic alcohol (1a) was employed in further investigations. The same transesterification reaction of 1a was conducted using lipase-ZrP under several different conditions (Entries 1–4, Table 1). In the reaction mixtures, \(\alpha\)-ZrP NS appear to be bound to lipases on the basis of physical interaction between adsorbed TPA\(^+\) on \(\alpha\)-ZrP NS and hydrophobic surface of lipases. In the cases of lipase-ZrP catalysts, substituting ZrP (toluene) for ZrP (toluene) (Entries 1 and 2) hardly changed the yield of allyl ester 2a. Hence, further experiments were conducted using the ZrP (THF) only (Entries 2–4). On the other hand, during the reactions described in entries 1 and 2, cotton-like white solids were observed in the reaction mixtures, suggesting the aggregation of \(\alpha\)-ZrP NS bound to lipase. Therefore, it was hypothesized that a diluted \(\alpha\)-ZrP NS solution may be preferable to achieve high dispersion and improved activity of lipase. Additionally, in the present study, the extra amount of TPA\(^+\) was used for the cation exchange capacity (CEC) of \(\alpha\)-ZrP (\(\eta_{\text{TPA}^+}/\text{CEC} = 1.2\) mol/mol) in order to exfoliate \(\alpha\)-ZrP, suggesting free TPA\(^+\) existed in the reactant solution and therefore may interfere progress of the reaction. In this regard, a diluted \(\alpha\)-ZrP NS solution is desirable. To maximize the yield of 2a, various amounts of ZrP (THF) were added to the reactants, and then the transesterification reactions of 1a were performed (Entries 2–4). A large amount of the ZrP (THF) (30 \(\mu\)L) was inappropriate to stimulate the reaction, as mentioned beforehand (Entry 2), and a small amount (5 \(\mu\)L) did not promote the reaction (Entry 4). As a result, the yield reached a maximum transesterification efficiency when 10 \(\mu\)L of ZrP (THF) was used (Entry 3). Consequently, the optimum amount was employed in following investigations. It was notable that the time required to complete the reaction in the presence of lipase-ZrP (Entry 3, 16 h) was reduced by two-thirds with comparable stereoselectivity when compared with that of free lipase (24 h), indicating the desirable impact of the \(\alpha\)-ZrP NS on the reaction process. The enhanced reaction rate suggested dispersion stabilization of lipase molecular with coexistence of \(\alpha\)-ZrP NS. Since \(\alpha\)-ZrP NS are not considered to behave as direct catalysts in the present transesterification reaction, the coexistence of lipase and \(\alpha\)-ZrP NS is necessary to accelerate the reaction rate. Binding to \(\alpha\)-ZrP NS may strengthen lipase that has a fragile molecular structure in nonpolar solvents. Therefore, the apparent catalytic activity of lipase will be improved in the presence of \(\alpha\)-ZrP NS.

[Scheme 1 & Table 1 near here]

Under the optimized reaction conditions, the effects of substituents on the aryl moiety in allylic alcohols were investigated as shown in Table 2. A methoxide substituent (MeO-) on the aryl moiety does not induce any significant improvement in both the yield and enantioselectivity upon addition of a suitable amount of ZrP (THF) (Entry 2). Judging from the low yields of 2c, substrates with bulkier side chains may be difficult to be trapped by a catalytic pocket of lipase as well as the tertiary...
alcohol 1b. To validate the prediction, the crystal structure of α-ZrP hybridized with lipases were evaluated by means of XRD (Figure 2). A broad diffraction band appeared at lower angle, indicating that a part of lipase molecules was embedded in internal space of house of cards structure composed of random stacking of nanosheet. Consequently, the substrates with bulky side chains might be difficult to approach to such internal lipases.

![XRD patterns of pristine α-ZrP powder and lipase-ZrP.](image)

**Figure 2.** XRD patterns of pristine α-ZrP powder and lipase-ZrP.

**Scheme 1.** Transesterification of racemic alcohols with lipase.

| Entry | Allylic ester | Allylic alcohol |
|-------|--------------|----------------|
| 1a    | Lipase-ZrP: 45%, 96% ee (16 h) | Lipase-ZrP: 44%, >99% ee (16 h) |
|       | Free lipase: 42%, >99% ee (24 h) | Free lipase: 47%, >99% ee (24 h) |
| 2a    | Lipase-ZrP: 27%, 92% ee (16 h) | Lipase-ZrP: 57%, 50% ee (16 h) |
|       | Free lipase: 30%, 88% ee (16 h) | Free lipase: 52%, 62% ee (16 h) |
| 3a    | Lipase-ZrP: 19%, 82% ee (16 h) | Lipase-ZrP: 31%, >99% ee (16 h) |
|       | Free lipase: 35%, 90% ee (16 h) | Free lipase: 63%, 68% ee (16 h) |

*All reactions were performed on a 2.0 mmol reaction scale using lipase 25 mg/mmol, 2 equiv isopropenyl acetate and 0.25 M ZrP (THF) in n-hexane (5 mL) at 40°C. Determined yield.*

Table 2. Substrate scope for transesterification of various secondary allylic ester derivatives with lipase-ZrP.

On the one hand, chiral allylic alcohol 1d and ester 2d with pyridyl moiety are frequently used in a part of molecular structures of important pharmaceuticals [23,24], ligands [25], nucleosides [26] and electronic materials, were also prepared with the same manner (Table 2, Entry 3). On the other hand, although the yield of 2d was reduced as a result of the hybridization with α-ZrP NS, the enantiopurity of (S)-1d remaining after the reaction was largely higher than that of free lipase. Based on electric polarity of a pyridyl ring (1d, 2d), a significant amount of products would be missed during flash chromatography using silica gel, causing the low yields of chiral products. By contrast, the substrates with simple structures (1a, 1d) seem to provide relatively high stereospecificity of both (R)-esters and (S)-alcohols. In generally, lipases have high enantioselectivity for ester hydrolysis and transesterification of racemic compounds. However, the selectivity often dependent on chemical structure of substrates because lipases have an asymmetric active pocket that is surrounded amino acid chains. In other words, 3D arrangements of those amino acid chains decide to reaction efficiency.

At present, it was confirmed that α-ZrP NS is effective in a limited substrate (1a) except for the high enantiopurity of (S)-1d. The proposed mechanism explaining the beneficial effects of α-ZrP NS on the lipase-catalyzed transesterification reaction is depicted in Scheme 3. Allylic alcohols may suffer deprotonation by the surface oxygen anions of α-ZrP NS bound to lipase. Then, the alcohols are transformed into corresponding alkoxides with higher nucleophilic activity that stimulates binding to a serine residue existing in a catalytic pocket with steric recognition ability only for (R)-alcohol (Scheme 4) [27]. Consequently, considerable

**Scheme 2.** A general reaction scheme of dynamic kinetic resolution of allylic alcohols.

**Scheme 3.** A plausible effect of α-ZrP NS for asymmetric transesterification of 1a.
improvement in the reaction rate of transesterification reaction might be achieved. In fact, the electron-donating substituent (1c) did not show any preferable enhancement of reaction efficiency as already stated, where a methoxide group is well-known to rise electron density of p-position. Thus, since degree of the deprotonation (i.e. pKa) of allylic alcohols must be dependent of electron-donating (or accepting) ability of substituents on the aryl moiety, an allylic alcohol with an electron-withdrawing group such as halogen should be employed and compared the yield and/or ee with others in order to validate the hypothesis. [Scheme 2–4 & Table 2 near here]

4. Conclusions

In the present study, we developed an efficient synthesis technique of chiral allylic esters using layered α-Zr(PO₄)₂⁺ (ZrP) nanosheets (NS) combined with lipase (lipase-ZrP). Initially, it was demonstrated that α-ZrP NS was stabilized in nonpolar solvents using tetrapentylammonium ions with relative high hydrophobicity as an exfoliating agent. The addition of an appropriate amount of α-ZrP NS facilitated the lipase-catalyzed transesterification reaction, especially for a simple allylic alcohol substrates. Although we cannot precisely explain why α-ZrP NS have such a beneficial effect on the lipase-catalyzed transesterification reaction in some cases, well dispersion and stabilization of lipase bound to α-ZrP NS would influence the enhanced reaction efficiency. Moreover, it was implied that deprotonation of allylic alcohols as a result of electrostatic interaction with surface oxygen anions of α-ZrP NS promoted the transesterification. In the near future, we will devote to elucidating the detailed mechanism for the increased catalytic activity by comparing reaction efficiencies among various allylic alcohols with different substituents.

Disclosure statement

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