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Ln-substituted polytungstates as efficient hetergeneous catalysts for Knoevenagel condensation reaction

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Three isomorphic polytungstates, $Cs_9K_{18}H_{10}\{[Sm_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}\cdot 46.5H_2O$ (**1**), $Cs_{10}K_9H_{18}\{[Eu_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}\cdot 41.5H_2O$ (**2**), $Cs_{10}K_9H_{18}\{[Gd_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}\cdot 46H_2O$ (**3**), have been successfully synthesized and characterized by routine methods, and demonstrated excellent catalytic activities in Knoevenagel condensation reaction as heterogeneous catalysts. Notably, catalyst **1** achieved higher reaction activity than catalysts **2** and **3**, where a satisfactory reaction yield (95%) and high TON value (6380) could be obtained at moderate reaction condition. In addition, in the scale-up experiment, with the help of catalyst **1**, 7.8 g benzaldehyde and 5.7 g ethyl cyanoacetate could transform into corresponding condensation product with a satisfactory yield (83%) and impressive TON value (13,883).

As one of the most important processes in synthetic organic chemistry and medicinal chemistry, Knoevenagel condensation reaction has received intensive attentions among the chemists for the convenient formation of the C—C bonds through condensing active methylene compounds and aldehydes (or ketones) [1–5]. The condensation products, α,β-unsaturated compounds, are widely used in many fields, such as pharmaceuticals, calcium antagonists, flavors, and fine chemicals [6–9]. Commonly, Knoevenagel condensation reactions are conducted under the participation of homogeneous basic catalysts, such as piperidine, ammonium salts, or K_2CO_3 [10,11]. However, these protocols suffer from some intrinsic drawbacks, including but not limited to weak reusability, harsh reaction conditions and pollutes generation, *etc*., which hurdle their practical applications [12,13]. These issues have been inspiring researchers to look for novel heterogeneous catalysts to circumvent aforementioned drawbacks. As a result, multiple catalysts have been developed for the Knoevenagel condensation reaction, such as metal-organic framework, ionic liquids, zeolites, graphene oxide [14–18] and polyoxometalates (POMs) [19–23].

POMs, as a kind of nano-sized metal-oxide clusters, were recently spotlighted in the field of catalysis and green chemistry, owing to their unique physicochemical properties and tunable structure [24–34]. Over the past two decades, there were some reports demonstrating POMs as ideal candidates in facilitating the Knoevenagel condensation reaction [19–23,35]. The study of POMs catalysts of Knoevenagel condensation reaction could date back to the 2007 [21], when Mizuno's group first reported that the basic POMs, $(TBA)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ and $(TBA)_7[H(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]$, could efficiently catalyze the condensation of benzaldehyde and malononitrile. Subsequently, they presented the highly negatively charged POMs $(TBA)_6[\gamma\text{-}H_2GeW_{10}O_{36}]$ could act as an excellent catalyst for Knoevenagel condensation reaction [22]. Inspired by mentioned work, Song *et al.* developed two trilacunary POMs showing satisfactory performance of the condensation reaction of ethyl cyanoacetate and benzaldehyde [36]. Aside from polytungstates catalysts, polyoxoniobates were also investigated as potential catalysts for Knoevenagel condensation reaction for their outstanding basicity [37–40]. In 2016, Tsukuda and Wang groups presented polyoxoniobates $(TMA)_6[Nb_{10}O_{28}]$ and $Na_{16}[SiNb_{12}O_{40}]\cdot xH_2O$ showing high catalytic activities for Knoevenagel condensation reaction, respectively [37,38]. After that, our group and Tsukuda group successively applied Lindqvist-type POMs, $K_7HNb_6O_{19}\cdot 13H_2O$ and $(TBA)_8[Ta_6O_{19}]$, in catalyzing the condensation reaction of benzaldehyde and ethyl cyanoacetate, and obtained satisfactory catalytic performances [39,40]. Compared to basic catalysts, catalysts containing Lewis acid and base sites are expected to give premium catalytic activities for their concurrent substrate activation and nucleophilic attack [41–44]. With that, transition-metal (TM) substituted POMs could be ideal catalysts towards Knoevenagel condensation reaction, where TM cores act as

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Lewis acid sites and nucleophilic surface-oxygen atoms work as the Lewis base sites, meanwhile their synergistic effect could be beneficial in accelerating the reaction process [45]. Based on this idea, very recently, our group reported polyoxomolybdates-based catalysts demonstrating impressivecatalytic activities in accelerating Knoevenagel condensation reaction due to the synergy of TM and POMs [19,20]. In addition, lanthanide (Ln) also have good Lewis acid ability, implying great potentials to further improve the performance of POMs-based catalysts though there are few related reports yet [45]. Therefore, we were strongly motived to explore novel Ln-substituted POMs from the viewpoints of both catalytic effect (design the satisfactory catalysts for Knoevenagel condensation reaction) and synthesis strategies (expand the POMs family).

Herein, we used simple POM $K_{14}[As_2W_{19}O_{67}(H_2O)]$ (abbreviate as $\{As_2W_{19}\}$) as the precursor, and successfully prepared three isomorphic Ln-substituted polytungstates: $Cs_9K_{18}H_{10}\{[Sm_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}\cdot 46.5H_2O$ (**1**) $Cs_{10}K_9H_{18}\{[Eu_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}\cdot 41.5H_2O$ (**2**) $Cs_{10}K_9H_{18}\{[Gd_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}\cdot 46H_2O$ (**3**) As hypothesized, these three POMs all showed satisfactory performance for gram-scale Knoevenagel condensation reaction. Particularly, the yield of 95% and the TON value of 6380 could be obtained in the presence of catalyst **1** (TON = turnover number, TON value = the mole conversion of ethyl cyanoacetate/the mole of catalyst used). The substrates screening and recyclability tests also demonstrated that **1** has excellent catalytic activity. In addition, we conducted the scale-up experiment to understand the practical application potential of **1**, where the yield and TON value of desired product was monitored as 83% and 13,883, respectively.

All three crystals were synthesized by routine hydrothermal method. The precursor $\{As_2W_{19}\}$ was prepared according to the literature [46]. The mixture of amino trimethylene phosphonic acid (ATMP, 0.36 mmol, 107.7 mg) and $\{As_2W_{19}\}$ (0.12 mmol, 633.6 mg) was dissolved in 15 mL H_2O, the pH of solution was maintained at 3.9 by 1 mol/L KOH. After the addition of $SmCl_3\cdot 6H_2O$ (0.12 mmol, 43.8 mg) and 0.1 g CsCl, we controled pH of this mixture at 5.8 by 1 mol/L KOH. Then, this solution was stirred and heated at 80 °C for another 1 h. Finally, the colorless block crystrals could be obtained by slow evaporation at room temperature about one week. Yield: 16.21% based on W. Elemental analysis (%) cacld. for **1** ($M_r = 19{,}028.75$): H, 0.65; C, 0.13; N, 0.07; P, 0.33; K, 3.70; As, 2.36; Cs, 6.29; Sm, 3.16; W, 59.90. Found; H, 0.52; C, 0.15; N, 0.06; P, 0.39; K, 3.82; As, 2.35; Cs, 6.32; Sm, 3.12; W, 60.12. IR (KBr, cm^{-1}): 3423 (br), 1623 (m), 1130 (w), 1085 (w), 950 (s), 858 (s), 783 (s), 717 (s), 628 (s). The preparation of compounds **2** and **3** (colorless block crystrals) were similar to that of compound **1**, and their synthesis were shown in Supporting information.

All of the reagents used were analytically pure and brought from commercial sources without further purification. Aldehydes (7.5 mmol), nitriles (5 mmol), catalyst (0.015 mmol%), and methanol (2.5 mL) were added into a tube at room temperature. Details of the reaction conditions are described in each result. The prepared mixture was stirred and heated at the designed conditions (80 °C, 800 rpm, and 3 h) in a WP-TEC-1020 parallel reactor from WATTCAS^{TM} (Fig. S5 in Supporting information). The product was qualitatively detected by GC–MS and the yield of the product was monitored by GC. After completion of the reaction, the catalyst was washed bymethanol (5 mL × 3) and then dried in an oven at 80 °C for 3 h.

Single-crystal X-ray diffraction analyses confirmed that the polytungstates **1-3** are isomorphic and all crystallized in the triclinic space group P-1. As a result, compound **1** was selected as a representative to discuss the structure in detail. Compound **1** is composed of nine Cs cations, eighteen K cations, forty-six point five water molecules, a

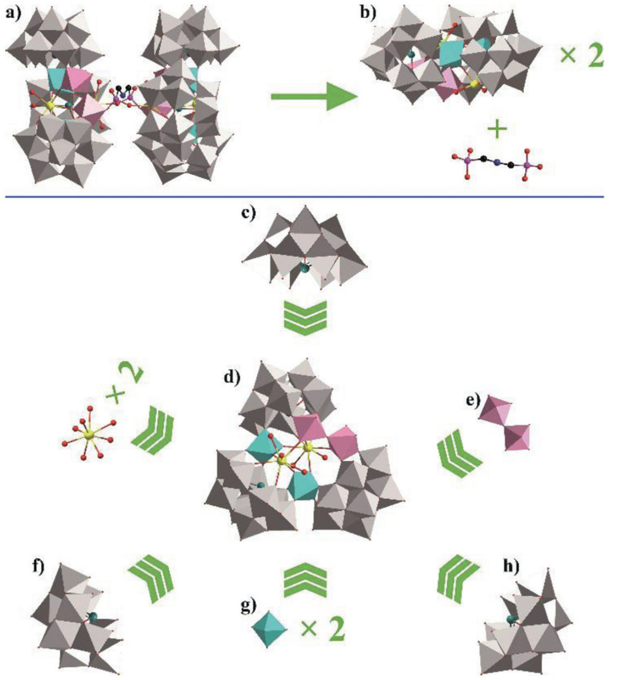


Fig. 1. Ball-and-stick and polyhedral representations of catalyst **1**. (a) Ball-and-stick and polyhedral representations of polyanion **1a**. (b, d) Ball-and-stick and polyhedral representations of $\{Sm_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3\}$. (c, f, h) Ball-and-stick and polyhedral representations of $\{AsW_9O_{33}\}$. (g, e) Polyhedral representations of $[WO_6]$ and $[W_2O_{11}]$, respectively. Color code: WO_6, gray-25% or aqua; W_2O_{11}, rose; As, teal; C, black; N, blue; P, pink; O, red; Sm, yellow.

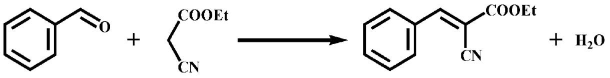
$\{[Sm_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3]_2(N(CH_2PO_3)_2)\}^{37-}$ (**1a**) polyanion (Fig. 1a) and ten protons. Polyanion **1a** consists of two identical $\{Sm_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3\}$ building blocks (Figs. 1b and d) and one organic-ligand $\{N(CH_2PO_3)_2\}$. Moreover, it could be condsidered as three tri-lacunary POMs $\{AsW_9O_{33}\}$ (Figs. 1c, f and h) interconnected together through two $[WO_6]$ (Fig. 1g) and one $[W_2O_{11}]$ (Fig. 1e) to form the skeleton of building block $\{Sm_2(H_2O)_4W_4O_{10}(AsW_9O_{33})_3\}$. Additionally, two Sm atoms (coordinated with eight O atoms) further bridge $\{AsW_9O_{33}\}$ and proximal $[WO_6]$ or $[W_2O_{11}]$ and maintain the structural stability. Crystallographic data and structural refinements of compounds **1-3** are listed in Table S1 (Supporting information).

According to the early reports, the Lewis acidity and alkalinity play significant roles in the catalytic process of Knoevenagel condensation reaction [41–44]. Therefore, we chose condensation reaction of benzaldehyde with ethyl cyanoacetate to evaluate the catalytic performances of compounds **1-3**. In this study, compounds **1-3** and their raw materials were investigated individually with results tabulated in Table S5 (Supporting information). In the blank experiment, the reaction proceeds in a very low yield (2%, Table S5, entry 1). The ATMP presents weak catalytic effect, while $LnCl_3$ and precursor $\{As_2W_{19}\}$ exhibit noteworthy catalytic performances, indicating the non-negligible contributions of Ln cores and POMs building blocks. Moreover, compounds **1-3** show great catalytic performances for Knoevenagel condensation reaction, among these catalysts, **1** gives the best result. With that, **1** was selected as the model catalyst to optimize the Knoevenagel condensation conditions reaction systematically.

The effects of catalyst loading, reaction temperature, and solvents were investigated using **1** to identify the premium reaction conditions. As shown in Table 1, when adding catalysts from 0.008 to 0.015 mol%, the yield and TON value of desire product show an upward trend (Table 1, entries **1-3**). However, both yield and TON value start to drop slightly when further adding catalysts (entry 4, 0.020 mol%), probably caused by the agglomerate of catalysts [47,48]. By comprehensive consideration of yield, TON value, and catalyst consumption, the optimal catalyst loading was locked at 0.015 mol%. Besides, reaction temperature at 80 °C is able to give the best catalytic performance (yield = 95%, TON value = 6380). As a result, 80 °C was decided as the suitable reaction temperature for further investigations. Moreover, the role of solvent is non-negligible and significant. Under the conditions of aforementioned influence factors, we also conducted the screening of solvent and summarized their results in Table 1, entries 1 and 7-10. It shows methanol could afford the desired product in excellent yields and splendid TON value, much better than reaction results carried out in acetonitrile and acetone representing non-protonic solvents. Non-polar solvents, such as *n*-hexane and toluene were also studied where the catalytic progresses hardly proceed well. In short, polar protonic solvent is beneficial in this catalytic progress, which is in good accord with reported literatures [19,20,43,49–51]. Furthermore, the catalytic activity of catalyst **1** was further verified by scale-up experiments to study its application potentials (Table 1, entries 12 and 13). Taking account of above results, the optimal conditions (Table 1, entry 1) had been determined for the subsequent catalytic evaluation. To benchmark the performance of catalyst **1**, we synthesized a reported POMs-based catalyst [19] (abbreviate as $[TeMo_6Co]_6$) and employed it to catalyze this process under the optimal reaction conditions as a reference (Table 1, entry 1 *vs.* 15). It clearly shows that catalyst **1** outperforms $[TeMo_6Co]_6$ in both product yield and TON values. Notably, to our best knowledge, catalyst **1** exhibits comparable or even better catalytic performance than reported catalysts in promoting Knoevenagel condensation reaction (Table 2), while maintaining a much higher TON value.

Encouraged by the above promising results, further studies of substrate scope were extended by employing different benzaldehydes and ethyl cyanoacetate under the optimal reaction conditions.

Table 1
Effects of the different factors in the Knoevenagel condensation reaction.[a]



Entry	Cat. (mol%)	Solvent	Yield[b] (%)	TON
1	0.015	methanol	95	6380
2	0.012	methanol	91	7617
3	0.008	methanol	85	10,750
4	0.020	methanol	93	4675
5	0.015	methanol	90	6007
6	0.015	methanol	93	6206
7	0.015	acetonitrile	35	2333
8	0.015	acetone	5	307
9	0.015	–	28	1838
10	0.015	*n*-hexane	trace	–
11	0.015	toluene	trace	–
12 [c]	0.015	methanol	76	12,733
13 [d]	0.015	methanol	83	13,883
14 [e]	**2**	methanol	94	6313
15 [f]	**3**	methanol	92	6160
16 [g]	$[TeMo_6Co]_6$	methanol	87	5840

[a] Reaction conditions: benzaldehyde (7.5 mmol), ethyl cyanoacetate (5 mmol), solvent (2.5 mL), 80 °C, 3 h, reflux conditions.

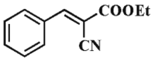
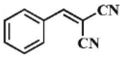
[b] GC yields for desired product were based on methylbenzene as internal standard. Obtained product was identified by GC–MS spectra, GC spectra and ^1H NMR.

[c, d] The scale-up experiments, reaction conditions: benzaldehyde (75 mmol), ethyl cyanoacetate (50 mmol), catalyst (0.006 mol%), CH_3OH (25 mL), 80 °C, [c] for 3 h ([d] for 5 h), reflux conditions.

[e, f] **2** and **3** as the catalysts under the optimal conditions.

[g] $[TeMo_6Co]_6$ = $(NH_4)_{17}Na_7H_{12}[Co(H_2O)TeMo_6O_{21}\{N(CH_2PO_3)_3\}]_6 \cdot 42H_2O$, 0.015 mol% [19].

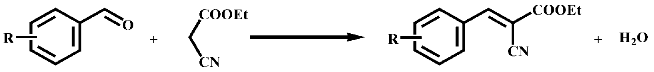
Table 2
Comparison of different catalysts for the Knoevenagel condensation reaction.

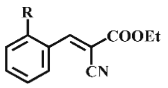
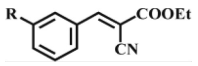
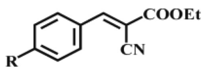
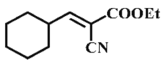
Entry	Catalyst	Product	*T* (°C)	Time (h)	Yield (%)	TON	Ref.
1	$[GeW_{10}]$		32	2	98	98	[20]
2	Na-A-PW_9		25	6	80	–	[24]
3	Na-B-PW_9		25	6	83	–	[24]
4	Cs-Beta-OF		60	3	52	–	[46]
5	$[Nb_{10}O_{28}]$		70	24	88	88	[25]
6	$Na_{10}SiNb_{12}O_{40}$		60	6	97	417	[26]
7	$K_7HNb_6O_{19}$		60	2	98	196	[27]
8	$[Ta_6O_{19}]$		30	8	99	–	[28]
9	Mg_3Al-PW_{12}		60	6	>99	33	[2]
10	$CoTeMo_6$		70	3	98	1960	[18]
11	$[TeMo_6Co]_6$		70	3	92	3067	[17]
12	**1**		80	3	95	6380	This work
13 [a]	$[TeMo_6Co]_6$		70	3	89	3216	[17]
14 [a]	**1**		80	5	83	13,883	This work
15	$[SiW_{10}O_{34}]$		32	2.5	90	180	[19]
16	$[SiW_{10}O_{32}]_2$		32	2.5	96	384	[19]
17	$[CdCl_2L]$		60	1	99	124	[52]
18	POVCOF		25	0.5	99	990	[53]
19	$K_7HNb_6O_{19}$		25	0.75	99	198	[39]
20	GO@Fe_3O_4@HybPOM		25	0.17	96	–	[54]
21	NH_{2-}MgAl-LDH-NS		40	1	96	–	[55]
22	PEI-C_{18}@SLPs@SiO_2		25	3	97	–	[56]
23	$CoTeMo_6$		25	0.25	99	1980	[20]
24 [b]	$EuFe^{III}Fe^{II}_6$		60	27	27	119	[57]
25 [b]	NUC-25		70	24	96	240	[58]
26 [b]	La_2O_3		70	2	81	–	[59]
27 [b]	Ce(70%)NaY		60	9	67	–	[60]
28 [b]	Pr(dpdo)		25	0.5	>99	166	[45]
29 [b]	PrV_{10}		25	0.5	88	147	[45]
30 [b]	**1**		25	0.15	98	6513	This work

[a] The scale-up experiments.

[b] Used catalysts were Ln-based catalysts.

Table 3
Reaction of various aldehydes with ethyl cyanoacetate over catalyst **1**.[a]

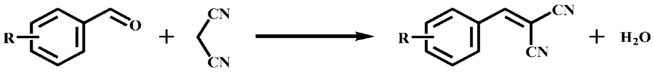


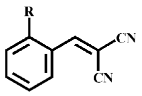
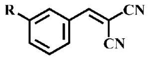
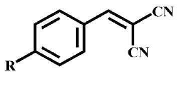
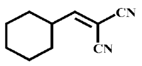
Entry	Product	-R	Yield [c] (%)	TON
1		$-NO_2$	99	6660
2 [b]		$-OCH_3$	89	5987
3		$-NO_2$	94	6660
4		-Cl	96	6467
5		$-NO_2$	99	6660
6		$-CH_3$	99	6660
7		-Cl	99	6640
8 [b]		$-OCH_3$	68	4567
9 [b]		–	84	5787

[a] Reaction conditions: aldehyde (7.5 mmol), ethyl cyanoacetate (5 mmol), catalyst (0.015 mol%), CH_3OH (2.5 mL), 70 °C, 3 h, reflux conditions.
[b] Reaction temperature 80 °C.
[c] GC yields for desired product were based on methylbenzene as internal standard. All obtained products were identified by GC–MS spectra and GC spectra.

Satisfactorily, the desired functional products could be obtained from Knoevenagel condensation reaction with high yields in the presence of **1** (Table 3). Particularly, we were also able to succeed in the transformation of sterically bulky *o*-methoxybenzaldehyde and *p*-methoxybenzaldehyde (Table 3, entries 2 and 8) into corresponding condensation product at a higher temperature (to compensate the steric hindrances). Moreover, hexahydrobenzaldehyde as a representative of non-aromatic aldehyde, was also able to react with ethyl cyanoacetate to form the condensation product in a satisfactory yield (84%, Table 3, entry 9). Following the study of condensation of various aldehydes with ethyl cyanoacetate, the Knoevenagel condensation reactions of various aldehydes with malononitrile were also investigated with their results summarized in Table 4. Catalyst **1** consistently demonstrates strong effectiveness regardless the substituents are located either in *para*, *meta*, or *ortho* positions: the catalytic progress could always be completed in excellent yields and splendid TON values within 15 min (Table 4, entries 1-9). Moreover, we also conducted the substrates screening for catalysts **2** and **3** and summarized their results in Tables S6−S9 (Supporting information). With that, we are convinced compound **1** is indeed an applicable and efficient catalyst in promoting Knoevenagel condensation reaction to form variable functional compounds.

Table 4
Reaction of various aldehydes with malononitrile over catalyst **1**.[a]



Entry	Product	-R	Yield [c] (%)	TON
1		-H	98	6513
2		$-NO_2$	99	6660
3		$-OCH_3$	97	6453
4		$-NO_2$	99	6660
5		-Cl	99	6660
6		$-NO_2$	99	6660
7		$-CH_3$	99	6660
8		-Br	98	6660
9		-Cl	99	6660
10 [b]		$-OCH_3$	94	6607
11 [b]		–	99	6607

[a] Reaction conditions: aldehyde (7.5 mmol), malononitrile (5 mmol), catalyst (0.015 mol%), CH_3OH (2.5 mL), 25 °C, 15 min, reflux conditions.
[b] Reaction temperature 60 °C, reaction time 1 h.
[c] GC yields for desired product were based on methylbenzene as internal standard. All obtained product was identified by GC-MS spectra and GC spectra.

Reaction reusability and reproducibility are another dimensional metrics evaluating the performance of a heterogeneous catalyst. The heterogeneity of catalyst **1** was validated by hot filtration experiment (Fig. S6 in Supporting information). Particularly, upon the catalyst removal, the reaction conversion rising trend is unsharp, proving the heterogeneous nature of this catalytic system. Reusability tests have also been performed to investigate their stability (Fig. S6). The easy separation of catalyst out from reaction mixtures using centrifugation method enables the catalyst to be recycled effectively.

Based on the relevant studies [61–64], a plausible catalytic mechanism was proposed for the Knoevenagel condensation reaction of benzaldehyde with ethyl cyanoacetate over the catalyst **1** (Fig. S8 in Supporting information). The catalytic progress starts with the interaction between basic sites and ethyl cyanoacetate, resulting in the abstraction of one acidic proton and the formation of a carbanion intermediate. Subsequently, this carbanion intermediate nucleophilically attacks the activated benzaldehyde that has been activated by Lewis acidic sites, allowing the generation of corresponding adduct (Step I). After that, the newly formed intermediate further transforms into desired product after eliminating a H_2O molecule (Step II) and catalyst **1** gets regenerated available for the next catalytic cycle.

In summary, three isomorphic Ln-substituted POMs have been successfully designed and synthesized through the conventional aqueous solution method. Satisfactorily, all three POMs present excellent performances in catalyzing gram-scale Knoevenagel condensation reactions along with good reaction reusability and reproducibility. Among them, catalyst **1** exhibits the best catalytic activity and outperforms most of the previously reported catalysts. More importantly, in the presence of catalysts, a wide scope of substrates could be effectively transformed into corresponding condensation products in satisfactory yields and TON values. Particularly, in the scale-up experiment, catalyst **1** achieves splendid performance (TON value = 13,883), which undoubtfully make itself a competent catalyst in promoting Knoevenagel condensation reaction in practical applications. Moving ahead, further efforts will be continuously devoted to design and develop practically efficient POMs-based catalysts with the hope to accelerate the adoption of POM chemistry in the fields of both scientific theory and engineering applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.108249.

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