

Sustainable Production of *o*-Xylene from Biomass-Derived Pinacol and Acrolein

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o-Xylene (OX) is a large-volume commodity chemical that is conventionally produced from fossil fuels. In this study, an efficient and sustainable two-step route is used to produce OX from biomass-derived pinacol and acrolein. In the first step, the phosphotungstic acid (HPW)-catalyzed pinacol dehydration in 1-ethyl-3-methylimidazolium chloride ([emim]Cl) selectively affords 2,3-dimethylbutadiene. The high selectivity of this reaction can be ascribed to the H-bonding interaction between Cl⁻ and the hydroxy group of pinacol. The stabilization of the carbocation intermediate by the surrounding anion Cl⁻ may be another reason for the high selectivity. Notably, the good reusability of the HPW/[emim]Cl system can reduce the waste output and production cost. In the second step, OX is selectively produced by a Diels–Alder reaction of 2,3-dimethylbutadiene and acrolein, followed by a Pd/C-catalyzed decarbonylation/aromatization cascade in a one-pot fashion. The sustainable two-step process efficiently produces renewable OX in 79% overall yield. Analogously, biomass-derived crotonaldehyde and pinacol can also serve as the feedstocks for the production of 1,2,4-trimethylbenzene.

The dwindling reserves of fossil resources, such as petroleum, coal, and natural gas, and increasing social concerns about global warming make it imperative to develop sustainable routes to produce renewable fuels and chemicals. Lignocellulosic biomass is among the most abundant and carbon dioxide-neutral energy sources that can be used as an alternative to conventional fossil feedstocks for the production of fuels^[1] and commodity chemicals.^[2–4] The past decade has witnessed substantial advances in this area. An elegant example is the production of *p*-xylene from biomass, involving a Diels–Alder (D–A) reaction and dehydration cascade of biomass-derived 2,5-dimethylfuran (DMF) with ethylene.^[3] Following this process, other valuable chemicals, such as aromatic carboxylic acids,^[4a–g]

toluene,^[4h] and styrene,^[4i] can also be obtained from bio-based furanics and dienophiles. Despite these impressive advances, the exploration of new sustainable routes to other bulk fossil-derived aromatics is still in great demand.

o-Xylene (OX) is a bulk chemical that is industrially produced by fractional distillation of xylenes from catalytic reforming of petroleum naphtha (Scheme 1). By recent estimation, the world demand for OX was approximately 6 million metric tons per year.^[5] Approximately 90% of OX is consumed in the preparation of phthalic anhydride, which is an important monomer for the industrial production of plasticizers for PVC products (e.g., bis(2-ethylhexyl) phthalate, DEHP), unsaturated polyesters, and alkyd resins. To fulfill the requirements of sustainable development, it is highly desirable to exploit a renewable process for the production of OX from biomass.

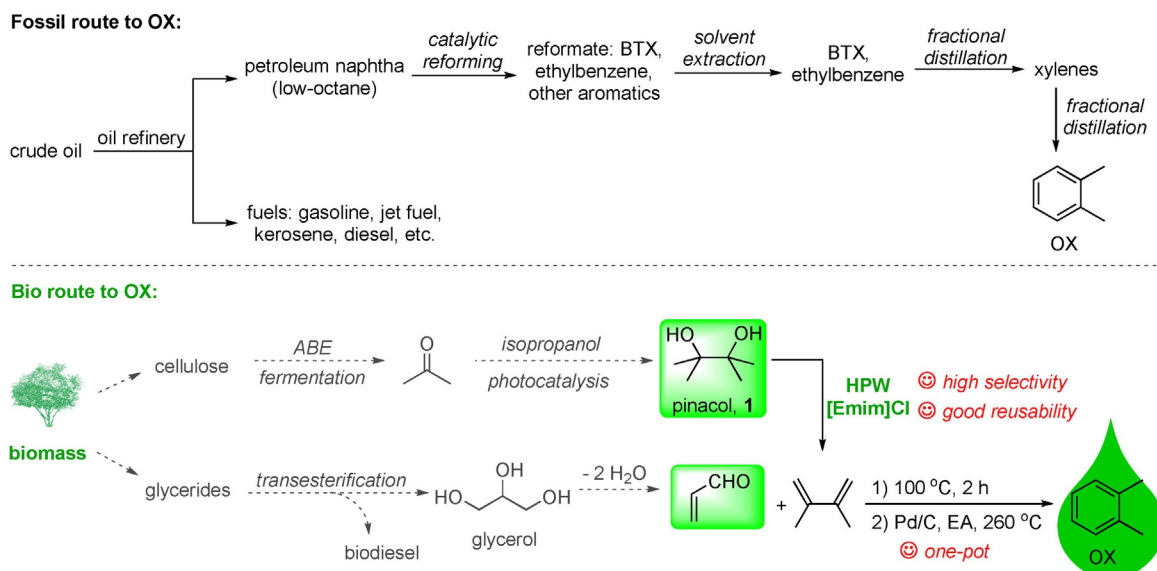
Pinacol is a renewable *vic*-diol that can be easily prepared by the metal-mediated coupling^[6] or electrolytic reduction^[7] of acetone from ABE (acetone–butanol–ethanol) fermentation of lignocellulose.^[8] Zhu and co-workers reported a sustainable photocatalytic coupling of isopropanol and acetone for the synthesis of pinacol.^[9] This approach is efficient and feasible because the hydrogen generated in the ABE fermentation step can be used to hydrogenate the acetone to give isopropanol. Acrolein, the simplest unsaturated aldehyde, can be efficiently formed by dehydration of glycerol, which is currently oversupplied as a byproduct of biodiesel production.^[10] Thus, developing new methods for the conversion of acrolein into bulk chemicals will be of great significance in enhancing the biodiesel economy. In this study, a two-step route for the synthesis of renewable OX was first developed using bio-based pinacol and acrolein as the feedstocks (Scheme 1). In the first step, the dehydration of pinacol selectively affords 2,3-dimethylbutadiene. This reaction is known to be very challenging because of the dominant pinacol rearrangement pathway.^[11] However, high diene selectivity is achieved in this work by employing 1-ethyl-3-methylimidazolium chloride ([emim]Cl) as the reaction medium and phosphotungstic acid (H₃PW₁₂O₄₀, abbreviated as HPW) as the catalyst. Moreover, the good recyclability of the HPW/[emim]Cl system can reduce the waste output and production cost. In the second step, OX is selectively produced by the D–A reaction of 2,3-dimethylbutadiene with acrolein and the following decarbonylation/aromatization cascade in a one-pot fashion.

The acid-catalyzed dehydration of pinacol has two competitive pathways: i) 1,2-elimination of H₂O to diene **2**; ii) pinacol rearrangement to pinacolone **3** (Table 1). In most cases, this reaction shows a preference for the pinacol rearrangement path-

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Scheme 1. A comparison of fossil- and bio-based routes to *o*-xylene (OX).

Table 1. Effects of solvent on HPW-catalyzed pinacol dehydration.^[a]

Entry	Solvent	EN T ^[b]	Yield of 2 [%] ^[c]	Yield of 3 [%] ^[c]
1	toluene	0.099	0	93
2	DMSO	0.444	38	13
3	NMP	0.355	17	8
4	[emim]Cl	–	88	5
5 ^[d]	[emim]Cl	–	N.R.	N.R.
6	–	–	0	79
7	[emim]NTf ₂	0.676	0	71
8	[emim]BF ₄	0.710	6	93
9	[emim]OAc	–	N.R.	N.R.
10	[emim]Cl	–	83	7
11	[pmim]Cl	–	63	4
12	[bmim]Cl	0.614	46	2
13	[hmim]Cl	0.562	N.R.	N.R.

R = Et, X = Cl, [emim]Cl R = propyl, X = Cl, [pmim]Cl
 R = Et, X = BF₄, [emim]BF₄ R = butyl, X = Cl, [bmim]Cl
 R = Et, X = NTf₂, [emim]NTf₂ R = hexyl, X = Cl, [hmim]Cl
 R = Et, X = OAc, [emim]OAc

pinacol, 75.18 ppm
 pinacol/[emim]Cl, 74.82 ppm
 pinacol/[emim]BF₄, 75.18 ppm
 pinacol/[bmim]Cl, 74.96 ppm
¹³C shift of C-1 atom

[a] Reaction conditions (unless otherwise stated): pinacol (1.0 g), HPW (100 mg), solvent (4.0 g), 130 °C, 16 h. [b] EN T scale was used to indicate the polarity of organic solvents and room-temperature ionic liquids. The values were obtained from ref. [13]. [c] Yields of **2** and **3** were detected by GC using tridecane as the internal standard. [d] Without HPW. DMSO = dimethyl sulfoxide; NMP = *N*-methyl pyrrolidone; N.R. = No Reaction.

way. In this regard, great efforts were devoted to increasing the diene selectivity. Heteropolyacids (HPAs) have been regarded as green and versatile solid acid catalysts to replace the conventional mineral acids.^[12] Therefore, we chose the Keggin HPA phosphotungstic acid (HPW) as the catalyst to test the solvent effects on the dehydration of pinacol. Just like many previous works,^[11] the dehydration of pinacol in a nonpolar solvent such as toluene favored the rearrangement pathway (Table 1, entry 1). However, it is surprising to find that the dehydration of pinacol in strong polar solvents, such as dimethyl sulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP), gave diene **2** as the main product, albeit in low yields (Table 1, entries 2 and 3). These results indicate that the polarity of the solvent seriously affects the dehydration patterns of pinacol.^[13] In view of the fact that ionic liquids (ILs) are endowed with strong electrostatic force and H-bonding interactions,^[14] we surmised that dehydration in ILs could possibly give a significant increase in the diene selectivity. As we expected, when the reaction was conducted in [emim]Cl, diene **2** was obtained in 88% yield and only trace amounts of pinacolone **3** were detected (Table 1, entry 4). In blank experiments using [emim]Cl or HPW alone (Table 1, entries 5 and 6), no diene **2** was formed, indicating that a synergistic effect of [emim]Cl and HPW is essential for the high diene selectivity. The influences of the anion and cation in the imidazolium-based ILs on the reaction were also investigated. When Cl[–] was exchanged for larger anions such as NTf₂[–] and BF₄[–], the main product switched from the diene to pinacolone (Table 1, entries 7 and 8). Furthermore, the dehydration did not occur in [emim]OAc (Table 1, entry 9). Interestingly, changing the solvent to 1-ethyl-2,3-dimethylimidazolium chloride ([emim]Cl), which bears a methyl group at the C2 position of the ring, afforded diene **2** in good yield (Table 1, entry 10). By varying the alkyl chain length on the cation of ILs, we found that longer-chain alkyl substituents resulted in a decreased diene yield (Table 1, entries 11–13; [pmim]Cl = 1-

propyl-3-methylimidazolium chloride). These results reveal that the chemoselectivity of diene **2** is strongly dependent on the chemical structure of the ILs.

According to previous reports, there are different H-bonding interactions between the cation and anion in neat ILs.^[14] In particular, the proton at the C2 position is more acidic than other hydrogens, which leads to the formation of a stronger H-bond with the anion (C2–H...X). However, after exposing pinacol to the ILs, the cation and anion of ILs also compete to interact with the hydroxy group of pinacol through hydrogen bond (C2–H...OH, X...HO), which might account for the increase of diene selectivity. According to the results we obtained, both [emim]Cl and [emmim]Cl enable good performances for the dehydration of pinacol to diene **2**. These results suggest that the interaction between Cl[−] and the hydroxy group of pinacol (Cl[−]...HO) plays a dominant role in controlling the diene selectivity, while the H-bond C2–H...OH is not crucial for the reaction. Besides the H-bonding interaction, the carbocation intermediate could also be stabilized by the surrounding anion Cl[−], which also contributes to the high diene selectivity. In contrast, the low selectivity of diene **2** in [emim]BF₄, [emim]NTf₂, and [emim]OAc can be explained by the weak interactions of the anions with the hydroxy group. The sterically hindered butyl group probably hampers the interaction between Cl[−] and pinacol, thus affording a low yield of diene **2** in 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Besides the steric hindrance of the hexyl group, the aggregation of 1-hexyl-3-methylimidazolium chloride ([hmim]Cl) may be another reason for the poor result achieved with that IL. It has been reported that with increasing alkyl chain length, ILs are more likely to aggregate, which limits the transfer of electrons and protons.^[15]

To further demonstrate the H-bonding interaction of pinacol and IL, additional NMR experiments were conducted. From the results given in Table 1, we can see that the ¹³C chemical shift of the C1 atom of pinacol in the mixture of [emim]Cl and pinacol moves upfield ($\delta = 74.82$ ppm, $\Delta\delta = 0.36$ ppm), whereas [emim]BF₄ exerts no influence on the chemical shift of pinacol. This phenomenon confirms that there is a H-bond between Cl[−] and the hydroxy group of pinacol (C_{im}⁺ Cl[−]...HO). Moreover, the mixture of [bmim]Cl and pinacol also gave rise to a decrease in the chemical shift of C1 ($\delta = 74.96$ ppm, $\Delta\delta = 0.22$ ppm), but its shift value was lower than that in [emim]Cl, because the bulky butyl group on the ring weakens the H-bond Cl[−]...HO, which leads to a low diene yield in [bmim]Cl.

Subsequently, the catalytic performances of other HPAs and tungstic acid were examined (Figure 1). Other commonly used Keggin-type HPAs such as phosphomolybdic acid (H₃PMo₁₂O₄₀, abbreviated as HPMo) and tungstosilicic acid (H₃SiW₁₂O₄₀, abbreviated as HSiW) were also found to be active for the reaction. The activity trend for the investigated HPAs was HPW > HSiW > HPMo, which is consistent with the trend in acid strength of these HPAs.^[16] Tungstic acid can also promote the dehydration but gave an inferior result.

We next studied the influence of the temperature on HPW-catalyzed pinacol dehydration (Figure 2). A high yield of diene **2** (88%) was obtained when the reaction was carried out at 130 °C for 16 h. With the increase of the temperature to 140 °C

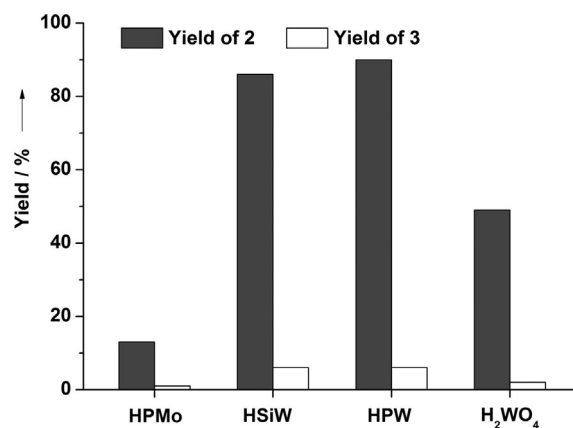


Figure 1. Yields of **2** and **3** over different acid catalysts. Reaction conditions: pinacol (1.0 g), catalyst (100 mg), [emim]Cl (4.0 g), 130 °C, 16 h.

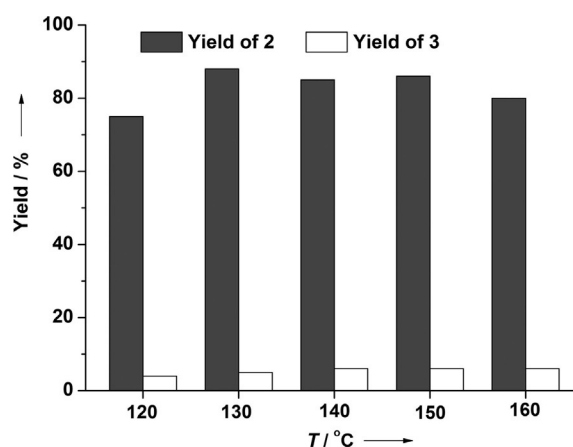


Figure 2. Yields of **2** and **3** over HPW over a range of reaction temperatures. Reaction conditions: pinacol (1.0 g), HPW (100 mg), [emim]Cl (4.0 g), 16 h.

or 150 °C, the yield of diene **2** remained comparable. However, after further increasing the temperature to 160 °C, a slight decrease in the yield of **2** was observed. This can be rationalized because excessive temperature resulted in the self-D–A reaction of diene **2** (see the Supporting Information, Figures S2, S17, and S18).

To fulfill the requirements for real application, the reusability of the HPW/[emim]Cl system for pinacol dehydration was tested (Figure 3). After each usage, the mixture spontaneously separated into two phases. The upper layer, containing diene **2** (GC purity > 94%), was isolated by decantation. The lower layer, containing [emim]Cl, HPW, and the byproduct water, was recovered by desiccation and reused in subsequent runs. From the result shown in Figure 3, the HPW/[emim]Cl system can be reused for at least four runs without significant loss in activity.

Having established the efficient synthesis of diene **2** from the selective dehydration of pinacol, we then directed our attention toward the solvent-free D–A reaction of diene **2** and acrolein to give 3-cyclohexenecarbaldehyde **5**, which was a potential precursor for the production of *o*-xylene (OX) by decarbonylation and aromatization (or dehydrogenation) reactions. According to our observation, the D–A reaction of diene **2** and

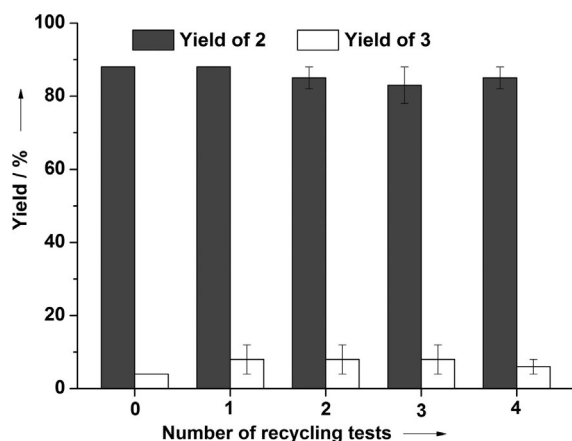


Figure 3. Yields of **2** and **3** over HPW through several recycling tests. Reaction conditions: pinacol (1.0 g), HPW (100 mg), [emim]Cl (4.0 g), 130 °C, 16 h.

acrolein can proceed spontaneously in the absence of solvent or catalyst. After being stirred at 100 °C for 2 h, diene **2** and acrolein were almost quantitatively converted into compound **5** (Figures S5, S19, and S20).

As the final aim of this work, we studied the production of renewable OX by a decarbonylation/aromatization cascade reaction of 3-cyclohexenecarbaldehyde **5** (Table 2). As Pd/C is known to be a highly active catalyst for both decarbonylation^[4e–g,17] and dehydrogenation,^[2h,18] we surmised that it may promote the the decarbonylation/aromatization cascade reaction of **5** to produce OX. This reaction proceeded at 260 °C under solvent-free conditions, although the OX yield was not very high (Table 2, entry 1). However, the addition of toluene

Table 2. Screening reaction conditions for the transformation of compound **5** into *o*-xylene **6** via decarbonylation/aromatization cascade.^[a]

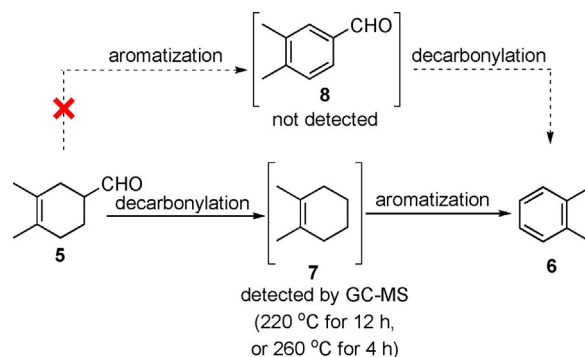
Entry	Catalyst ^[b]	Solvent	T [°C]	Yield of 6 [%] ^[c]
1	Pd/C	–	260	48
2	Pd/C	toluene	260	88
3	Pd/C	THF	260	87
4	Pd/C	EA	260	97
5	Pd/C	H ₂ O	260	0
6	Pd/C	EA	240	69
7	Pd/C	EA	220	31
8	Pt/C	EA	260	78
9	Ru/C	EA	260	N.R.
10	Ir/C	EA	260	N.R.
11	Ni/C	EA	260	N.R.
12	Raney Ni	EA	260	39

[a] Reaction conditions: compound **5** (0.28 g, 2.0 mmol), catalyst (28 mg), solvent (0 or 20 mL), argon atmosphere, 600 rpm, 12 h. [b] The catalysts were obtained from commercial sources and the metal content of the supported catalysts was 5% by weight. [c] Yields were detected by GC using tridecane as the internal standard. THF = tetrahydrofuran; EA = ethyl acetate; N.R. = No Reaction.

or THF as solvent significantly improved the OX yield (Table 2, entries 2 and 3). Gratifyingly, 97% yield of OX was achieved when the reaction was conducted in ethyl acetate (Table 2, entry 4), a renewable solvent that can be produced through esterification of biomass-derived ethanol and acetic acid. In contrast, the use of H₂O as a green reaction medium failed (Table 2, entry 5). The temperature also exerted a great influence on the OX yield over Pd/C. With a decreased temperature of 240 °C or 220 °C, lower OX yields were obtained (Table 2, entries 6 and 7).

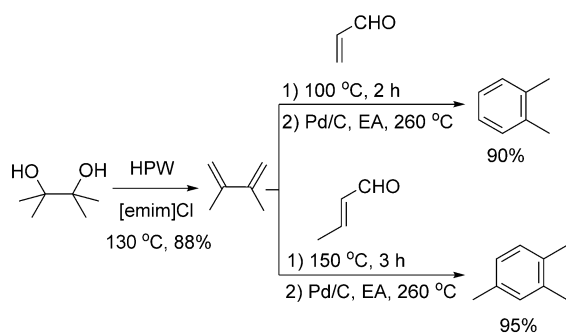
The catalytic activity of other metals for this cascade process was further assessed. Besides Pd/C, Pt/C and Raney Ni were also found to be active for the process although their activities were lower than that of Pd/C (Table 2, entries 8 and 12). In contrast, the Ru/C, Ir/C, and Ni/C catalysts were totally inactive under the investigated conditions (Table 2, entries 9–11).

To investigate the reaction pathway, we performed the decarbonylation/aromatization cascade of compound **5** over Pd/C catalyst at 220 °C. Decreased reaction temperature led to a lower OX yield and the appearance of 1,2-dimethylcyclohex-1-ene **7** in the products (Figure S7), whereas 3,4-dimethylbenzaldehyde **8** was not identified in the mixture. This phenomenon indicates that the reaction first undergoes decarbonylation, followed by aromatization to generate OX (Scheme 2). To further confirm this pathway, we conducted the reaction at 260 °C for 4 h and detected 1,2-dimethylcyclohex-1-ene **7** in the mixture as well (Figure S8). From the results, we can also discern that the aromatization of **7** is the rate-determining step in this process.



Scheme 2. Possible reaction pathway for the conversion of compound **5** into OX.

We also tried to combine the D–A reaction and the following decarbonylation/aromatization cascade in a one-pot reaction (Scheme 3). To do this, a mixture of 2,3-dimethylbutadiene and acrolein was first stirred at 100 °C for 2 h. Ethyl acetate and Pd/C were then added in sequence and the system was stirred at 260 °C for 12 h. As we expected, a high yield (90%) of OX was achieved by this method. This is advantageous for real application, because the need to isolate compound **5** can be avoided, which will further improve the efficiency and economy of the process. Taking into account the optimum diene yield in the first step, the renewable OX was produced in 79% overall yield from pinacol and acrolein by a two-step route.



Scheme 3. A sustainable two-step route for the production of renewable o-xylene and 1,2,4-trimethylbenzene.

Crotonaldehyde is another commonly used unsaturated aldehyde that can be prepared by the self-aldol condensation of biomass-derived acetaldehyde. 1,2,4-Trimethylbenzene (TMB) is a bulk chemical that is widely used as a gasoline additive and a precursor to trimellitic anhydride for the production of plasticizers for PVC products, such as tri(2-ethylhexyl) trimellitate (TOTM) and polyester resins. Analogously, a two-step route for the production of renewable 1,2,4-trimethylbenzene from pinacol and crotonaldehyde was also proposed (Scheme 3; for detailed information, see the Supporting Information, Figures S11 and S12). A high overall yield of 1,2,4-trimethylbenzene (83%) was achieved through this sustainable process.

In summary, we have developed an efficient and sustainable two-step route for the production of OX from biomass-derived pinacol and acrolein. In the first step, HPW-catalyzed pinacol dehydration in [emim]Cl selectively afforded 2,3-dimethylbutadiene. The utilization of [emim]Cl as solvent significantly improved the 2,3-dimethylbutadiene selectivity, which can be ascribed to the H-bonding interaction between Cl^- and the hydroxy group of pinacol. Stabilization of the carbocation intermediate by the surrounding anion Cl^- may be another reason for the high selectivity. Notably, the good reusability of the HPW/[emim]Cl system can reduce the waste output and production cost. In the second step, the D–A reaction of 2,3-dimethylbutadiene with acrolein and the following Pd/C-catalyzed decarbonylation/aromatization cascade were successfully combined into a one-pot fashion. The intensified two-step process could efficiently produce renewable OX in 79% overall yield. Analogously, biomass-derived crotonaldehyde and pinacol can also serve as the feedstocks for the production of 1,2,4-trimethylbenzene.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: acrolein · biomass conversion · cascade reactions · heteropoly acids · ionic liquids

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