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A Simple and Mild Approach for the Synthesis of *p*-Xylene from Bio-based 2,5-Dimethyfuran by Metal Triflates in Ionic Liquids

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Abstract: The production of aromatic platform chemicals from biomass-derived feedstocks is of great importance in biomass conversion. However, developments of effective routes with simple steps and mild conditions are still challenging. In this work, we reported a novel route to directly synthesize *p*-xylene from 2,5-dimethylfuran and acrylic acid by Sc(OTf)₃ in [Emim]NTf₂ at mild conditions, overall 63% selectivity of *p*-xylene and 78% selectivity of aromatics were obtained at 90% conversion of 2,5-dimethylfuran by enhancing the dehydration and introducing an extra one-pot decarboxylation process. Furthermore, various dienes and dienophiles were employed as reactants to extend the substrate scope and the aromatics were obtained with moderate yields, which proved the potential of the method to be a generic approach for the conversion of bio-based furanics into renewable aromatics.

Introduction

Terephthalic acid (TA) is an important bulk chemical in industry, which serves as the precursor of polyethylene terephthalate (PET). PET is used to produce various containers related to our daily life, such as beverage bottles, barrels of edible oil, synthetic fibers and so on.^[11] In decades, global market of TA from liquid-phase oxidation of petro-derived *p*-xylene (PX) has been demonstrated healthy growth due to increasing demand of PET industry. However, the conventional production of PX has raised a lot of environmental issues and chronically lagged behind its surging demand. Meanwhile, the depletion of fossil fuels directly lead to the dwindling supply of crude oil, it becomes rather urgent to explore alternative raw materials and sustainable processes for the production of PX.

Biomass, a widespread, abundant and renewable resource, is considered as one of the most promising renewable feedstock to produce chemicals and energy used to be produced from fossil fuels. For example, aromatic compounds and fuels can be obtained via catalytic fast pyrolysis of solid biomass (e.g. wood, agricultural wastes) and depolymerization of lignin.^[2] It can be expected that the fraction of chemicals and energy supplied by

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renewable biomass will inevitably increase in coming years. Recently, a lot of research aiming at converting biomass into renewable TA and PX has been reported,^[3] either dealing with the effectiveness and stability of catalysts or focusing on exploring new alternative routes.

As ethylene can be derived from bioethanol, Brookhart et al. reported a strategy to use ethylene as the only feedstock to produce PX, the trimerization, dehydrogenation, Diels-Alder (DA cycloaddition and dehydrogenation catalyzed by multiple catalysts afforded PX as final product.[4] Other routes to renewable TA and PX mainly focused on the processes starting from 5-hydroxymethylfurfural (HMF) and its derivatives, for example, the Diels-Alder cycloaddition and subsequent dehydrative aromatization between ethylene and 2.5furandicarboxylic acid (FDCA) from fully oxidization of HMF. However, the electron-poor properties of FDCA result in a deactivated diene, and ethylene is inherently unreactive unless high pressure and high temperature conditions are applied to the reaction. Davis et al. has reported that the reaction of FDCA with high pressure ethylene over Sn-beta zeolite was extremely slow and only negligible yield of product was detected at 210 °C for 12 h, while much better aromatic yields were obtained for the reaction of other oxidized deriviates of HMF and ethylene.^[5] To some degree, the intrinsic limitations from FDCA to TA motivate the research efforts into the production of PX from 2,5dimethylfuran (DMF), another biosourced furanic compound from the hydrogenation of HMF.^[6] Dauenhauer et al. firstly investigated the application of H-Y zeolite as catalyst for the conversion of DMF and ethylene into PX via Diels-Alder cycloaddition and dehydration reaction.^[7] The confinement within the zeolites was considered to promote the cycloaddition while the dehydration was catalyzed by the Brønsted acid sites. Subsequently, different beta zeolites (e.g. H-, Zr-, Sn-beta) were investigated by several groups for their application on the reaction of DMF and ethylene,^[8] and a highest yield of 97% was obtained over a P-containing beta zeolite at 99% conversion of DMF at 250 °C, 6.2 MPa for 24 h.^[9] In a recent breakthrough, ethanol was directly used as the source of dienophile to generate ethylene to react with DMF in a one-pot reaction over HUSY-12 without high pressure condition at 300 °C. Moreover, the use of ethanol resulted in higher reaction rate and aromatic selectivity over Brønsted zeolites owing to the formation of protonated water molecular from ethanol dehydration.^[10] Another alternative strategy reported by Xu et al. is to produce diethyl terephthalate which can be used as a precursor of PET to replace TA from biomass-derived muconic acid, the two-step synthetic route including esterification/Diels-Alder reaction and dehydrogenation reaction were catalyzed by silicotungstic acid and Pd/C respectively. The esterification process was found to be crucial as it improved the reactivity of muconic acid and ethylene, the overall yield was 80.6% at 200 °C.[11]

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As known, high temperature and pressure conditions are hardly to be avoided with ethylene as the dienophile, the attempts to use other abundant and cost-effective dienophiles are of real significance. Acrolein, acrylic acid and maleic anhydride can all be efficiently produced from biomass, hence they become promising alternatives of ethylene.^[12] Toste et al. demonstrated the feasibility of PX production from DMF and acrolein, giving 34% yield of PX via Diels-Alder, oxidation, dehydration and decarboxylation cascade reactions, -60 °C was required in order to suppress the activity of retro Diels-Alder reaction.^[13] Lobo et al. synthesized 2,5-dimethylbenzoic acid (2,5-DMBA) from DMF and acrylic acid over Hf-beta and mixed anhydride (i.e acetyl methanesulfonate) by a two-step protocol with moderate yield.^[14] Of particular interest, a facile solid phase reaction was studied by van Es et al. for the aromatization of hydrogenated DA adducts of DMF and maleic anhydride, the aromatization proceeded faster without any solvent and was accompanied by full decarboxylation to produce 11% vield of PX over H-Y zeolite at 200 °C.[15] Nevertheless, the requirements of either high temperature or low temperature and multiple reaction steps in these routes are new challenges remaining to be solved.

As a new type of high-efficient green media, ionic liquid has gained rapid development in recent years.^[16] It is reported that various Diels-Alder reactions can be accomplished in ionic liquids, with higher selectivity and fast reaction rate.^[17] On the other hand, metal triflates were regarded as versatile catalysts for various reactions including the Diels-Alder and dehydration reaction of DMF and ethylene.^[18] Moreover, metal triflates are mostly water sensitive while ionic liquids have the advantage that moisture sensitive agents could be used so that the combination of metal triflates and ionic liquids may be a promising catalytic system for the tandem Diels-Alder and dehydration reactions.

Herein, we investigated the application of metal triflates in the reaction of DMF and acrylic acid to produce PX in ionic liquids, shown in Scheme 1. For the first part reaction (red line in Scheme 1), screening of catalysts and solvents demonstrated that Sc(OTf)₃ was the most efficient and [Emim]NTf₂ serves as an excellent solvent which resulted in large rate enhancement and selectivity promotion by stabilizing the catalytic active compounds. With further study of several co-catalysts, H₃PO₄ showed good performance on improving the dehydration efficiency and aromatic yield. Furthermore, this system was verified to be effective for the reactions using different substrates. Then for the second part (blue line in Scheme 1), a viable decarboxylation process was carried out subsequently in onepot reaction in order to obtain higher PX productivity, the formed 2,5-DMBA and unreacted precursors in the first step reaction can be further converted into PX. The current research was considered to propose an alternative route for transforming biomass-derived platform compounds into renewable aromatics, particularly PX.



Scheme 1. One-pot route to renewable PX from DMF and acrylic acid in this work.

Results and Discussion

Optimization of reaction parameters

The metal triflates have been reported as excellent catalysts for some Diels-Alder reactions and dehydration reactions,^[18c, 18d, 19] Therefore, they were firstly employed as catalysts in this reaction. It was found that the reaction was preferred to be carried out with excessive acrylic acid in solvent-free condition, and the reaction times for different catalysts were optimized, shown in Table 1.

As expected, all the metal triflates investigated here were demonstrated to be effective for this reaction with moderate yields of PX and 2,5-DMBA (Figure S1, S2). Acid strength of

 Table 1. The conversion of DMF and acrylic acid into aromatics by different catalysts.^[a]

| Catalyst | Time (h) | Conv. (mol%) | Yield (r | nol%) | Total aromatic | |
|----------------------|----------|-----------------|----------|-------|----------------|--|
| | | | 1 | 2 | (mol%) | |
| Sc(OTf) ₃ | 1 | 93 | 31 | 17 | 48 (52) | |
| Sc(OTf)3[b] | 1 | 88 | 23 | 13 | 36 (41) | |
| Sc(OTf)3[c] | 1 | 89 | 22 | 16 | 38 (43) | |
| Cu(OTf) ₂ | 5 | 90 | 29 | 16 | 45 (50) | |
| Yb(OTf) ₃ | 12 | 92 | 28 | 18 | 46 (49) | |
| Y(OTf) ₃ | 24 | 90 | 32 | 15 | 47 (52) | |
| CuCl ₂ | 24 | 3 | 0.6 | 0.4 | 1 (33) | |
| CuBr ₂ | 24 | 35 | 2 | 10 | 12 (35) | |
| Blank ^[d] | 24 | 0 | 0 | 0 | 0 (0) | |

[a] Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), catalyst (0.05 mmol), 15 °C. [b] In CH₂Cl₂ (0.5g). [c] In CHCl₃ (0.5g). [d] Without catalyst.

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these metal triflates had little influence on the aromatic selectivity and Sc(OTf)₃ and Y(OTf)₃ exhibited slightly better performance compared with others. On the other hand, the reaction rate showed large dependency on the Lewis acid strength. Sc(OTf)₃ was the most efficient catalyst with the shortest reaction time to achieve up to 90% conversion of DMF due to its highest Lewis acidity. On the contrary, the reaction rate was the slowest using Y(OTf)₃ which has the weakest Lewis acid strength.^[18c, 20] Further attempts to decrease the catalyst loading to 0.02 mmol were made using Sc(OTf)₃ and Y(OTf)₃ respectively. However, moderate conversion (64%) was obtained using Y(OTf)₃ for 24 h and prolonging the reaction time did not give a higher conversion, while the reaction proceeded again with further addition of Y(OTf)₃ to the reactor implying that the deactivation of Y(OTf)₃ occurred in this process. Importantly, this was not observed when Sc(OTf)₃ was used as catalyst, similar product yield was achieved in 3 h in comparison to the results in entry 1. Table 1. thus the catalytic stability of Sc(OTf)₃ was better than Y(OTf)₃. Subsequently, by varying the anion of the metal salts, CuCl₂ and CuBr₂ showed substantially less effective, low yields of aromatics were obtained, which may properly be attributed to their low acidity not enough to activate the dienophile via interaction with the carbonyl oxygen.^[21] Based on the results, Sc(OTf)₃ was the most excellent catalyst and used for further investigation.

Diels-Alder reaction was normally thermodynamic controlled and the reactant concentration has dramatic effects on the reactivity,^[13, 22] thus the variation of the acrylic acid/DMF ratio was studied. The yield of aromatics (4% to PX, 2% to 2,5-DMBA) was quite low when using excessive amount of DMF (acrylic acid/DMF=1/5.2) at the identical condition. Sc(OTf)₃ was not soluble in DMF and it was fouled as indicated by colour change in DMF, thus unknown interactions between DMF and Sc(OTf)₃ may exist to suppress the catalytic activity. Higher acrylic acid/DMF ratio was found to be beneficial for the reaction, shown in Figure 1. The yield of PX increased with the increase of acrylic acid/DMF ratio firstly and then it reached a plateau when the acrylic acid/DMF ratio was up to 6.9. Surprisingly, the yield of 2,5-DMBA showed no dependency on acrylic acid/DMF ratio and remained constant. The oxanorbornene intermediate of DMF and acrylic acid (intermediate 3 in Scheme 2) was



Figure 1. The conversion of DMF and product yields with various ratios of acrylic acid/DMF. Reaction condition: DMF (1 mmol), corresponding amount of acrylic acid, $Sc(OTf)_3$ (0.05 mmol), 15 °C, 1 h.

identified (Figure S2) and significant amount of **3** without dehydration was observed in all the reactions here suggesting that the dehydration was the limiting step in the production of 2,5-DMBA. Normally, higher acrylic acid concentration could drive the Diels-Alder equilibrium to give higher yield of **3**, whereas, the amount of **3** did not increase when increasing acrylic acid dosage. Considering the yield of PX increased instead of 2,5-DMBA, it could be deduced that the formation of PX could possibly also consume **3** and **3** was a precursor of both PX and 2,5-DMBA. The reaction pathway to PX was more efficient compared with the pathway to 2,5-DMBA in this condition.

Since the conversion includes Diels-Alder, dehydration and decarboxylation reactions, it was influenced by multiple factors. The influence of temperature on this reaction was studied, shown in Table 2. Diels-Alder cycloaddition has been reported to be resistant to high temperature condition due to its reversibility and exothermicity, low temperature condition could help to suppress the retro Diels-Alder reaction and reduce starting material decomposition hence leading to an increased yield of DA adduct.^[22] Then the dehydration and decarboxylation reactions are normally enhanced by increasing temperature. Notably, the outcomes of the reactions carried out at 15 °C and 40 °C were similar which could exactly be explained by these combined effects. The yield of DA adduct at 40°C was lower than that at 15 °C while the aromatization was more efficient at 40 °C, resulting in the same aromatic selectivity at the two temperatures. Additionally, larger amount of 3 without dehydration was observed at 15°C revealing that the Diels-Alder cycloaddition proceeded more easily compared with the dehydration, thus the dehydration efficiency needed to be improve in order to obtain higher aromatic yield. Whereas, with the increase of temperature, the yields of the aromatics decreased and more side products were detected. As the reaction intermediates like 3 are very unstable and sensitive to heat, they can polymerize easily in the presence of acid,^[14] a lot of unknown compounds are inevitably synthesized with time

Table 2. The effect of temperature on the reaction of DMF and acrylic acid in solvent free condition. $\ensuremath{^{[a]}}$

| Temperature (°C) | Conv. | Yield (ı | mol%) | Total aromatics |
|------------------|---------|----------|-------|-----------------|
| | (1101%) | 1 | 2 | (mol%) |
| -10 | 92 | 39 | 16 | 55 (60) |
| 15 | 93 | 31 | 17 | 48 (52) |
| 40 | 94 | 31 | 18 | 49 (52) |
| 65 | 95 | 25 | 15 | 40 (42) |
| 90 | 93 | 11 | 13 | 24 (26) |

[a] Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), Sc(OTf)₃ (0.05 mmol), reaction time: 24 h (-10 °C), 1 h (15 °C), 0.5 h (40 °C, 65 °C, 90 °C).

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Scheme 2. Simplified reaction pathway for the conversion of DMF and acrylic acid into PX and 2,5-DMBA.

particularly at a higher reaction temperature. Overall, severe side reactions diminished the enhancement of aromatization at higher temperature. Whereas, it is interesting that the reaction could even proceed when acrylic acid turned to be frozen at -10°C.

Furthermore, an alcohol compound (intermediate **4**) was also identified by GC-MS analysis, shown in Scheme 2 (Figure S2). Actually, it is an isomer of the well-known oxanorbornene precursor of PX in the reaction of DMF and ethylene, and it is also a precursor of PX.^[23] As the decarboxylation of 2,5-DMBA was reported to occur at 210 °C over Cu-based catalyst, normally it is hardly to proceed at -10 °C.^[13] A comparative experiment using 2,5-DMBA in CH₂Cl₂ with Sc(OTf)₃ at room temperature was carried out, as expected it further proved the infeasibility of decarboxylation starting from 2,5-DMBA. Since **3** was also a precursor of PX, we hypothesize that **3** can be decarboxylated to **4** and the subsequent dehydration of **4** yielded PX.

Even though the one-step conversion of furanics into aromatics has been successfully achieved over metal triflates, too many side reactions lead to relatively low aromatic yield. Besides, the severe polymerization of acrylic acid in acidic solvent free condition also raise problems.^[24] It becomes necessarily to explore alternative ways to stabilize the active intermediates and inhibit acrylic acid polymerization in order to improve aromatic yield and reduce the waste of raw materials.

Improvement by using ionic liquids as the solvent

The application of ionic liquids on Diels-Alder reaction was reported to avoid low temperature condition required to suppress the retro Diels-Alder reaction.^[25] Various ILs with different cations and anions were employed as the solvents for this reaction, the results are shown in Figure 2.

It was found that [Emim]NTf₂ was the best solvent to give the highest aromatic selectivity. The anions of ionic liquids greatly influence the reaction, and ionic liquids with $[NTf_2]$ ⁻ were preferred solvents which can significantly accelerate the reaction with a lower catalyst loading (1.5 mol%) and improve the product selectivities at room temperature. $[NTf_2]$ ⁻ salts were hydrophobic and miscible with reactants, thus water formed in the reaction pathway could be conveniently removed from the reaction phase, which promoted the dehydration of intermediates and prevented the deactivation of Sc(OTf)₃ by water. Even though the amount



Figure 2. The effect of ILs with different anions and cations on the reaction. Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), ionic liquid (1.5 mmol), Sc(OTf)₃ (0.015 mmol), 15 $^{\circ}$ C, 0.5 h.

of **3** was considerably reduced with the addition of [Emim]NTf₂, it is interesting that only PX yield was significantly improved while the yield of 2,5-DMBA was almost the same as the results in ionic liquid free conditions. Therefore, the related interactions between PX precursors and [Emim]NTf₂ may lead to more selective results of PX, the reaction pathway to PX was more efficient than the pathway to 2,5-DMBA, intermediate **3** was largely consumed by PX production and this phenomenon exactly coincided with the results when increasing the acrylic acid/DMF ratio.

On the other hand, by varying the alkyl substituent on the cations of ionic liquids, the long alkyl substituent led to lower selectivity, which could be explained by the unfavourable steric interaction between catalytic active species (i.e. reaction intermediates) and ionic liquids to stabilize the intermediates.^[26] Moreover, when the alkyl chain are longer than four carbons, the

| Table 3 | . The | effect | of tem | perature | e on t | he | reaction | of | DMF | and | acrylic | acid | in |
|---------|----------------------|--------|--------|----------|--------|----|----------|----|-----|-----|---------|------|----|
| [Emim]N | √Tf ₂ .[a | 1] | | | | | | | | | | | |

| Temperature (°C) | Conv. | Yield (mo | ol%) | Total aromatics | |
|------------------|---------|-----------|------|-----------------|--|
| | (1101%) | 1 | 2 | (mol%) | |
| -10 | 81 | 40 | 16 | 56 (69) | |
| 0 | 94 | 40 | 19 | 59 (63) | |
| 15 | 87 | 43 | 16 | 59 (68) | |
| 40 | 89 | 34 | 18 | 52 (58) | |
| 65 | 89 | 23 | 9 | 32 (36) | |
| 90 | 84 | 17 | 10 | 27 (32) | |

[a] Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), [Emim]NTf₂ (1.5 mmol), Sc(OTf)₃ (0.015 mmol), reaction time: 10 h (-10 °C), 3 h (0 °C), 0.5 h (15 °C), 10 min (40 °C), 5 min (65 °C, 90 °C).

aggregation behaviour of ILs is much more significant and limits the transfer of electrons and protons intramolecularly.^[27] As reported, the strength of hydrogen bonding between ionic liquid and dienophile also played an essential role in the activation of dienophile hence the reaction rate and selectivity.^[28] However, [Bmim]PF₆ and [Bmim]BF₄ containing efficient hydrogen bond accepting anions gave poor yields of the desired products and some unknown side products were observed using [Bmim]PF₆.

The effect of temperature was also carried out over Sc(OTf)₃ in [Emim]NTf₂ as shown in Table. 3. Contrary to the results obtained in ionic liquid free conditions, lowering temperature did not exert obvious promotion on aromatic selectivity. This unexpected results were presumably due to the changes of related interactions between intermediates and [Emim]NTf2, as the properties of ionic liquids may change a lot at low temperature.^[29] With an increase of temperature, the yield of either PX or 2.5-DMBA decreased and the decrease of PX yield was much more significant, revealing that the decarboxylation was more sensitive to temperature in [Emim]NTf₂. Another obvious phenomenon at higher temperature was the severe side reactions, 2,5-hexanedione, the hydrolyzed product of DMF, was the main side product, and other side products derived from alkylation and coupling of PX and DMF were also detected since Sc(OTf)₃ is an efficient catalyst for such kinds of reactions as well.^[30] Besides, some unknown side products with high boiling points were also detected (Figure S1).

Reaction kinetics

In order to get more insights into the reaction dynamics, the reaction was monitored as a function of time in Figure 3. DMF reacted with acrylic acid rapidly and the selectivities of PX and aromatics were up to 63% and 78% in the initial stage of the reaction. Subsequently, the aromatic selectivity decreased significantly when the conversion was up to 30% and the PX yield reached the highest point at 30 min, which indicated that the desired products could not exist stably under the reaction condition. Moreover, a certain amount of **3** and **4** was observed at 30 min, either prolonging the reaction time or increasing the amount of $Sc(OTf)_3$ to 0.05 mmol could not dehydrate them into



Figure 3. Conversion of DMF and product yield as a function of time. Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), [Emim]NTf₂ (1,5 mmol), Sc(OTf)₃ (0.015 mmol), 15 °C.



Figure 4. Kinetics on the conversion of DMF catalyzed by $Sc(OTf)_3$ in [Emim]NTf₂ at 15 °C to 65 °C. Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), [Emim]NTf₂ (1.5 mmol), $Sc(OTf)_3$ (0.015 mmol).

the desired aromatics. Therefore, the catalyst deactivation and insufficient reaction time were not the reasons for the inefficient progression of dehydration, the catalytic system required further improvement.

Based on the results above, the experiments monitoring DMF conversion at other temperatures were carried out to obtain the kinetic parameters (Table S6). DMF was consumed with the first-order reaction law from 15 °C to 65 °C and an apparent activation energy (E_a) of 33.1 ± 3.6 kJ/mol (7.9 ± 0.85 kcal/mol) was obtained in Figure 4 (Table S7), which seemed to be a far too low value for this reaction. Actually, Davis et al. has reported a very low apparent E_a for the reaction of DMF and ethylene due to multiple factors related to the effective rate constant.^[8c] Similarly, the retro Diels-Alder reaction and a number of side reactions occurred, the measured E_a was the results of the combined effects of multiple terms. Even though this obtained E_a was not the precise value for the desired reaction, the low value still suggested the highly active reaction and it could properly explain the reactions proceeding smoothly at -10 °C in the frozen phase.

Co-catalyst and one-pot decarboxylation process

As previously reported, 4Å molecular sieve (4Å MS) was a good co-catalyst for the dehydration of 3.[13] However, no product was detected when 0.1 mg 4Å MS was added to the reaction for 5 h. Since 4Å MS was a widely used drying agent, the water content in the reaction phase was firstly considered to be the crucial factor. Actually Lobo et al. reported the "on water" effect of Diels-Alder reaction between furan and maleic anhydride, minimal amount of water was able to influence the selectivity, and Windmom et al. found rate increase by adding water in this reaction.^[22] However, it becomes impossible to determine whether the reported "on water" effect applies for this system as Sc(OTf)₃ is water sensitive. For other possibilities, water may play an irreplaceable role in the reaction mechanism and the reaction was unable to proceed smoothly without it. Otherwise, the reaction may start to take place inside the zeolites rather than in the solution with the addition of 4Å MS, leading to the

| Table 4. The effect of additional dehydration agents on the reaction. ^[a] | | | | | | | | | |
|--|---------|-----------|------|-----------------------|--|--|--|--|--|
| Co-catalyst | Conv. | Yield (mo | ol%) | Total aromatics yield | | | | | |
| | (1101%) | 1 | 2 | | | | | | |
| 4Å MS ^[b] | 1 | 0 | 0 | 0 | | | | | |
| H_2SO_4 | 97 | 6 | 17 | 23 (24) | | | | | |
| H ₃ PO ₄ | 71 | 46 | 19 | 65 (92) | | | | | |
| $H_3PO_4^{[c]}$ | 87 | 48 | 22 | 70 (80) | | | | | |
| $H_3PO_4^{[d]}$ | 33 | 11 | 5 | 16 (49) | | | | | |

[a] Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), [Emim]NTf₂ (1.5 mmol), Sc(OTf)₃ (0.015 mmol), co-catalyst (0.5 mmol), 15 °C, 0.5 h; [b] 0.1 mg; [c] 1 h; [d] Without Sc(OTf)₃.

extremely slow reaction rate. Latter, H_3PO_4 and H_2SO_4 were chosen as dehydration additives, shown in Table 4. Poor aromatic selectivity was obtained when using H_2SO_4 due to its strong oxidizability. Gratifyingly, 46% yield of PX and 19% yield of 2,5-DMBA were obtained at 71% conversion of DMF at 15 °C for 0.5 h with the addition of 0.05 mmol H_3PO_4 , the aromatic selectivity was increased from 68% (Table 3, entry 3) to 92%. With prolonging the reaction time to 1 h, the aromatic yield increased to 70% with a decrease of selectivity to 80%. Recently, the P-containing materials were reported to selectively catalyze the dehydration reaction of DMF and ethylene without performing the alkylation and oligomerization side reactions, and PX can be obtained with above 40% yield using H_3PO_4 as



[a] Reaction conditions: DMF (1 mmol), acrylic acid (6.9 mmol), Sc(OTf)₃ (0.05 mmol), 15 °C, 1 h and subsequently Cu₂O (0.1 mmol), 4,7-diphenyl-1,10-phenanthroline (0.2 mmol), 1-methyl-2-pyrrolidinone (1.5 ml), quinolone (0.5ml) were added, 210 °C, 4 h; [b] All regents were added in one-step; [c] Without H₃PO₄ in the first step.

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homogeneous acid catalyst solely.^[9] Since the yields of two aromatic products increased and little amount of **3** and **4** were detected after adding H₃PO₄ to the reaction, the use of H₃PO₄ here greatly promote the dehydration thus further improve the product selectivity. Regrettably, some side reaction still occurred after 0.5 h and the reaction time needed to be longer when adding H₃PO₄, which may be attributed to the partial deactivation of Sc(OTf)₃ by the water content in H₃PO₄ solution.

Nevertheless, the mixed products (48% yield of PX and 22% yield of 2,5-DMBA) obtained will lead to costly separation process in further industrialization, it would be better to convert 2,5-DMBA to PX and obtain a single product stream. As a result an extra decarboxylation was applied to this reaction,^[13, 31] the results were listed in Table 5. Interestingly, the attempt to perform the reaction in one-step by adding all the regents and catalysts to the reactor initially failed to give a good PX yield, while the PX yield increased to 57% when conducting the reaction in one-pot and two-step sequence. Few side products intermediates were detected suggesting that the and intermediates observed at the end of first-step reaction may be further converted into desired products without forming side products during the decarboxylation at 210 °C. It was on the opposite of the results in the study of temperature effect on the first-step reaction in which severe side products formed when increasing reaction temperature. Thus the catalyst and solvents added in the decarboxylation step could help to suppress the unwanted side reactions at higher temperature. On the other hand, acrylic acid was found to be mostly transformed into ethylene in the decarboxylation process, Sc(OTf)3 can also catalyze the reaction between DMF and ethylene, which may also contribute to the increased PX yield.[18c] However, 2,5-DMBA left after the decarboxylation for 4 h cannot be fully converted by either prolonging the reaction time to 6 h or increasing the dosage of decarboxylation catalyst while acrylic acid can be completely converted, thus we speculated that a reaction equilibrium about 2,5-DMBA may exist at 210 °C. Also from entry 3, Table 5, the yield of aromatics did not get significantly improved with the addition of H₃PO₄, it was reasonable since the intermediates can mostly be converted into aromatics without H₃PO₄ in the decarboxylation process.

Substrate scope

For further exploration of the scope of the reaction, the application of the $Sc(OTf)_3$ and $[Emim]NTf_2$ system on other starting materials was investigated, the reactions studied were presented in Scheme 3 and the results were summarized in Table 6.

The desired aromatic products were obtained from the reactions using 2-methylfuran and furan as the dienes to react with acrylic acid, even though the aromatic yield was lower compared to the reaction of DMF and acrylic acid. When using maleic anhydride as the dienophile, higher amount of ionic liquid was used in order to make the mixing better in [Emim]NTf₂. In the reaction of DMF and maleic anhydride, the full decarboxylation was achieved with 3% yield of PX, three products obtained in one-step at 50 °C in this reaction were

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Scheme 3. Study of substrate scope using different reactants.

identical to that reported via a solid phase reaction at 200 °C.^[15a] Since the dehydration and decarboxylation of DA adduct of DMF and maleic anhydride were hardly to occur in traditional solvents because of retro Diels-Alder reaction,^[15b] it can be concluded that the stabilization of DA adducts and elimination of retro Diels-Alder reaction were well conducted by the use of ionic liquid. Moreover, it was different from the research of van Es *et al.* that toluene was also obtained which suggested the existence of full decarboxylation in the reaction of 2-methylfuran and maleic anhydride.^[32]

| Table 6. Conversion of different substituted furanics and dienophiles. ^[a] | | | | | | | | |
|---|-----------|------|---------|-----|-----------------|---------|--|--|
| Diene | Conv. (%) | Mola | r yield | (%) | Total aromatics | | | |
| | | 5 | 6 | 7 | 8 | (mol%) | | |
| X=CH ₃ ,Y=H | 91 | 12 | 2 | 9 | - | 23 (26) | | |
| X=Y=H ^[b] | 89 | 4 | 22 | - | - | 26 (30) | | |
| X=Y=CH ₃ | 22 | 3 | 3 | - | 11 | 17 (77) | | |
| X=CH ₃ ,Y=H | 24 | 3 | 0 | 2 | 11 | 16 (66) | | |

[a] Reaction conditions: for the reactions using acrylic acid: diene (1 mmol), acrylic acid (6.9 mmol), [Emim]NTf₂ (1.5 mmol), Sc(OTf)₃ (0.015 mmol), 15 $^{\circ}$ C, 0.5 h; for the reactions using maleic anhydride: diene (1.2 mmol), maleic anhydride (1 mmol), 25 $^{\circ}$ C, 2 h and then [Emim]NTf₂ (2.5 mmol), Sc(OTf)₃ (0.05mmol) were added, 50 $^{\circ}$ C, 10 h; [b] Sc(OTf)₃ (0.05mmol), 50 $^{\circ}$ C, 5 h.

Conclusions

In summary, we have demonstrated that metal triflates were capable of converting DMF and acrylic acid into PX and 2,5-DMBA in ionic liquids at mild conditions, 68% aromatic selectivity was obtained in one-step over Sc(OTf)₃ in [Emim]NTf₂. The addition of a co-catalyst, that is H_3PO_4 , improved the aromatic selectivity to 80%~92%. In order to further convert 2,5-DMBA into PX, an extra one-pot decarboxylation process was employed in this reaction, 57% yield and 63% selectivity of PX

was achieved without optimization. Finally, we successfully confirmed the generality of this method using various substrates. This work represents an important approach to access high value aromatic products from renewable feedstocks and the further work will focus on the improvement of catalyst and also the in-depth mechanistic understanding.

Experimental Section

The reactions were conducted in a vial (25 ml) with a magnetic stirring bar, ionic liquid (1.5 mmol), acrylic acid (6.9 mmol) and corresponding amount of catalysts were loaded into the reactor, and then the reactor was purged with N₂ by using a vacuum/ N₂ cycle (x4), the mixture was kept in a 15 °C water bath and diene (1 mmol) was added into the reactor. For the reaction at lower temperature, ethanol bath was used. When using maleic anhydride, diene (1.2 mmol) and maleic anhydride (1 mmol) were mixed and stirred at 25 °C for 2 h, then [Emim]NTf₂ (2.5 mmol) and Sc(OTf)₃ (0.05mmol) were added to the reactor to start the aromatization for 10 h at 50 °C in N₂ atmosphere.

For the one-pot and two-step reaction containing extra decarboxylation process,^[13, 31] Cu₂O (0.1 mmol), 4,7-diphenyl-1,10-phenanthroline (0.2 mmol), 1-methyl-2-pyrrolidinone (1.5 ml and quinoline (0.5ml) were added to the reactor at the end of the reaction of DMF and acrylic acid catalyzed by Sc(OTf)₃, then all the reaction media was transferred into a stainless steel batch type reactor equipped with a magnetic stirrer. The air in the reactor was replaced with N₂ and the reaction was stirred at 550 rpm at 210 °C for 4 h.

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Keywords: *p*-xylene • biomass • cycloaddition • aromatics • ionic liquid

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Entry for the Table of Contents

FULL PAPER



Renewable *p*-xylene was directly synthesized from biomass-derived 2,5dimethylfuran and acrylic acid over $Sc(OTf)_3$ and H_3PO_4 in [Emim]NTf₂ at mild conditions, and a subsequent one-pot decarboxylation process further gave overall 63% selectivity of *p*-xylene at 90% conversion of 2,5-dimethylfuran. Lingli Ni, Jiayu Xin,* Huixian Dong, Xingmei Lu, Xiaomin Liu and Suojiang Zhang*

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A Simple and Mild Approach for the Synthesis of *p*-Xylene from Bio-based 2,5-Dimethyfuran by Metal Triflates in Ionic Liquids