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Green synthesis of 1-phenyl-1-*ortho*-xylene ethane in IL and reaction mechanism†

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1-Phenyl-1-*ortho*-xylene ethane (PXE) in IL was synthesized, and the catalysts used were AlCl_3 in 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) or 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), and H_2SO_4 . When the concentrations of AlCl_3 in IL, *ortho*-xylene and styrene were 0.35, 0.03 and 0.005 mol, respectively, it could be discovered that ([BMIM][Br]) was the best catalyst. When the mole fraction concentration of AlCl_3 /[BMIM][Br] was more than 0.40%, the reaction was able to achieve 100% conversion. When the reaction time was longer than 60 minutes, the percentage conversion of *ortho*-xylene attained was 100%. The mechanisms of the reaction were investigated by the DFT method at the B3LYP/6-311++G(d, p) level. The potential energy surface (PES) profile indicated that the energy of transition state was 22.59 kcal mol⁻¹. This indicated that the activation energy of reaction was 28.24 kcal mol⁻¹, which illustrated that the reaction occurred easily. Vibrational frequencies were observed in FT-IR spectra, the corresponding vibrational modes $\nu_s(\text{H4-C3Al-H5})$ and $\nu_{as}(\text{H4-C3Al-H5})$ indicated that an Al^{3+} ion was combined with a C3 atom. In addition, the repeated use of the catalysts was studied; the ionic liquids could still catalyze the reaction and the percentage yield of PXE was larger than 91% after 6 runs.

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1. Introduction

1-Phenyl-1-*ortho*-xylene ethane (PXE) and bis(1-phenyl ethanyl) *ortho*-xylene (BPXE) are synthesis liquids with excellent performance because of their high boiling points, low viscosity, high solubility, low melting points, high-color printer's ability, high dielectric strengths and electrothermal stability, *etc.*, and are widely used in pressure sensitive dye solvents of carbonless paper and electrical insulating oil. In addition, they can also be used as a plasticizer, transformer oil, and other high boiling point solvents. Current commercial alkylation processes are catalyzed primarily by concentrated sulfuric acid or hydrofluoric acid.¹ The reaction equation is as follows:

The sulfuric acid process produces large amounts of spent acid and acid-soluble oils, which cause serious environmental problems. Anhydrous HF is highly toxic and its leakage produces dangerous stable aerosols at the ground level. In addition, equipment corrosion, transport, hazard management and environmental liability associated with the disposal of

spent acids are disadvantages of both processes. To avoid pollution a more environmentally friendly catalyst is desired.^{2,3}

Room temperature ionic liquid (IL) systems have many unique properties such as a very large liquid temperature range, and they can be made task-specific for certain applications,⁴ which include use as solvents in chemical synthesis and catalysis⁵⁻¹¹ and separation technology,^{12,13} as electrolytes in electrochemical devices,¹⁴⁻¹⁶ and as lubricants or as heat-transfer fluids.¹⁷ In addition, there is a huge range of possible combinations of cations and anions, which contribute to the design of ILs.¹⁸ However, before these liquids can be used commercially on an industrial scale, the process variables need to be optimized in the laboratory, not only in batch and continuous reactor systems for maximum reactant conversion, but also the product yield and catalyst selectivity. Previous studies have demonstrated that the activity of such systems strongly depends on the molar ratio of AlCl_3 /IL. Usually, maximal activity can be obtained at a molar ratio of 1.5–2.0 of AlCl_3 to IL.^{19,20}

This study reports that 1-phenyl-1-*ortho*-xylene ethane (PXE) is synthesized in IL and the catalysts used are AlCl_3 in 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) or 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]). The reaction mechanism presented in this work is drawn in the following scheme.

The catalytic activity of a Lewis acid-IL is studied under different experimental conditions, such as different catalysts, concentrations, temperatures and reaction times. The catalysts are facily isolated from products and effectively recycled. The mechanism of the reaction is determined using quantum

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chemical calculations and vibrational frequencies are observed in FT-IR spectra. The repeated use of the catalysts is also investigated.

2. Experiments

2.1 Materials

High-purity *ortho*-xylene, styrene and anhydrous AlCl_3 were used in this study and purchased from the Tianjin Damao Chemical Reagent Factory (Tianjin, China) and Chinese Medicine Group Chemical Reagent Co, Ltd (Beijing, China). [BMIM][Cl] (CAS no. 79 917-90-1) and [BMIM][Br] (CAS no. 85 100-77-2) were purchased from the Lanzhou (Lanzhou, China) Center for Green Chemistry with a purity of 99% and water mass fractions of less than 10^{-3} (g g^{-1}). To remove traces of volatile compounds, the ILs were kept in a vacuum (about 10^{-6} bar) at 343 K for 24 h prior to use.

2.2 Apparatus and measurements

An Agilent 6890 (Agilent Co. USA) gas chromatograph equipped with a flame ionization detector (FID) was employed for analysis. The detector temperature was maintained at 240 °C. The column was programmed with an initial temperature of 60 °C and this was increased thereafter to 220 °C at a rate of 15 °C min^{-1} . The column used for this purpose was HP-1 with dimensions of 50 m $\times$ 0.25 mm $\times$ 0.50 μm .

To support the computational results, Fourier transform infrared (FT-IR) spectra of 2BP8HQ were recorded using a Nicolet iS5 FT-IR spectrometer (4000–525 cm^{-1} ; number of scans: 250; resolution: 1 cm^{-1}) to study the variations of the IR spectra of *ortho*-xylene and styrene, and the reaction processes.

2.3 Computational methods

The reactant (R), intermediate (IM) and transition states (TS) and formed products (P) were fully optimized using the B3LYP/6-311++G(d, p) basis set, containing polarizable and diffuse functions, and this well described the weak interactions in the binary systems, especially for intermolecular H-bonded interactions. The interaction energy (DE) was estimated by employing the counterpoise (CP) method for the Gaussian basis set superposition error (BSSE).²¹ From intrinsic reaction coordinate (IRC) calculations and the potential surface (PES) energy profile for the transition state, two desired minima states of the mechanism were obtained. All the DFT calculations were carried out using the Gaussian09 package.²²

3. Results and discussion

3.1 Solubility of AlCl_3 in [BMIM][Cl] and [BMIM][Br]

A given amount of anhydrous AlCl_3 is slowly added to 3.00 g of [BMIM][Cl] and [BMIM][Br] and the mixture is stirred at different temperatures until the catalyst is completely dissolved. AlCl_3 /[BMIM][Cl] and AlCl_3 /[BMIM][Br] ionic liquids are thus obtained. The solubility of AlCl_3 in [BMIM][Cl] and [BMIM][Br] is shown in Table 1. It can be seen that the solubility of AlCl_3 increased with the increase of temperature. The solubility of AlCl_3 in [BMIM][Br] is higher than that in [BMIM][Cl]. The saturation points of AlCl_3 in [BMIM][Cl] and [BMIM][Br] are around 50 °C and 80 °C, respectively. Experimental results also show that the solubility of AlCl_3 in [BMIM][Cl] and [BMIM][Br] is larger in the latter than in the former. Since the catalytic properties of these binary mixtures depend on their acidities, we can conclude that the catalytic activity of the latter is

Table 1 Solubility of AlCl₃ in [BMIM][Cl] and [BMIM][Br]

Temp. (°C)	[BMIM][Cl]			[BMIM][Br]		
	Solution ^a	Content ^b	Solubility (%)	solution ^a	Content ^b	Solubility (%)
20	0.00056	0.029792	0.0330	0.00643	0.31936	0.4628
30	0.00061	0.032366	0.0350	0.00719	0.344118	0.5249
40	0.00068	0.035947	0.0400	0.00824	0.375501	0.6015
50	0.00075	0.039501	0.0430	0.00862	0.386132	0.6292
60	0.00078	0.041016	0.0450	0.00877	0.390229	0.6402
70	0.00078	0.041016	0.0450	0.00900	0.396406	0.6570
80	0.00078	0.041016	0.0450	0.00952	0.409921	0.6950
90	0.00078	0.041016	0.0450	0.00952	0.409921	0.6950

^a The concentration is the mole concentration. ^b Molar content of AlCl₃ ($X(\text{AlCl}_3) = ([\text{AlCl}_3]/([\text{AlCl}_3] + \text{IL}))$).

stronger than the former, which can be adjusted by the molar ratio of AlCl₃/IL.

3.2 Effects of different catalysts on the reaction

Different catalysts were added to, under the conditions of stirring, solutions of styrene and *ortho*-xylene dropwise; the reaction is performed in an 80–85 °C oil bath. TLC (petroleum ether as a solvent) was used to monitor the progress of the reaction. After the completion of the reaction, the reaction liquid was left standing and allowed to cool; the lower layer was separated. The ionic liquid catalyst is rapidly added to small amounts of *ortho*-xylene for the next use. *ortho*-Xylene is distilled and recovered, and the distillation product is collected at 208–214 °C.

When the concentration of AlCl₃ in IL, *ortho*-xylene and styrene are 0.35, 0.03 and 0.005 mol, respectively, the reactions are performed at 30 °C, the effects of different catalysts on the reaction are shown in Table 2. It can be seen that the orders of yield are AlCl₃/[BMIM][Br] (99%) > AlCl₃/[BMIM][Cl] (73%) > H₂SO₄ (56%), which indicated that the yields of AlCl₃ in [BMIM][Cl] and [BMIM][Br] are larger than that of H₂SO₄, especially, the yield of AlCl₃/[BMIM][Br] reaches 99%. This illustrates that AlCl₃/[BMIM][Br] is the best catalyst for the alkylation reaction of *ortho*-xylene and styrene. Hence, AlCl₃/[BMIM][Br] is used as the catalyst in the following experiments.

3.3 Effects of different mole fractions of AlCl₃/[BMIM][Br] on the reaction

When the amount of *ortho*-xylene and styrene is 0.03 and 0.005 mol, respectively, the reactions are carried out at 30 °C,

and the effect of the different mole fractions of AlCl₃/[BMIM][Br] on the reaction is listed in Table 3. It can be seen that the percentage conversion of *ortho*-xylene increased with the increase of the mole fraction of AlCl₃/[BMIM][Br], and when the mole fraction of AlCl₃/[BMIM][Br] is larger than 0.40%, the percentage conversion of *ortho*-xylene attained was 100%. This shows that as long as the mole fraction concentration of AlCl₃/[BMIM][Br] is more than 0.40%, the reaction will be able to achieve 100% conversion, and moreover, the rates of formation of PXE and BPXE increased with the increase of the mole fraction of AlCl₃ to [BMIM][Br]. The ¹H NMR spectrum for a mixture of PXE and BPXE with a 1 : 0.36 ratio is shown in Fig. S1 (ESI†). ¹H NMR (500 MHz, CDCl₃): δ 7.35–7.20 (m, 3 + 2.13H), 7.20–7.10 (m, 4 + 1.42H), 7.08–6.90 (m, 1 + 0.71H), 4.27 (q, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 0.71H), 2.29 (s, 3H), 2.21 (s, 2.13H), 2.18 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 2.13H), 1.58 (d, *J* = 7.2 Hz, 3H). The results are in agreement with the data in ref. 23.

3.4 Effects of different temperatures on the reaction

When the amount of *ortho*-xylene and styrene was 0.03 and 0.005 mol, respectively, the reaction time was 60 minutes and the mole fraction of AlCl₃/[BMIM][Br] was 0.40%. The reactions were carried out, and the effects of different temperatures on the reaction are given in Table 4. It can be seen that the percentage conversion of *ortho*-xylene increased with the increase of temperature, and when the temperature is higher than 60 °C, the percentage conversion of *ortho*-xylene attained is 100%. This illustrates that 60 °C is enough for the reaction. At the same time, the rates of formation of PXE and BPXE

Table 2 Effects of different catalysts on the reaction^a

Entry	Catalyst	Time (min)	Conversion (%)	Selectivity (%)		Yield ^b (%)
				PXE	BPXE	
1	H ₂ SO ₄	60	45	47.6	9.5	56
2	AlCl ₃ /[Bmim][Cl] ^c	60	85	57	16	75
3	AlCl ₃ /[Bmim][Br] ^c	60	100	69	30	98

^a Reaction conditions: *ortho*-xylene (0.03 mol), styrene (0.005 mol) and catalyst (0.5 g) at 30 °C. ^b GC yield was shown. ^c The mole ratio of AlCl₃ to IL is 0.35.

Table 3 Effects of different mole fractions of $\text{AlCl}_3/[\text{Bmim}]\text{Br}$ on the reaction^a

Entry	$\text{AlCl}_3/[\text{Bmim}][\text{Br}]$ (mole ratio)	Time (min)	Conversion (%)	Selectivity (%)		Yield ^b (%)
				PXE	BPXE	
1	0.28	60	24	24	1.3	17
2	0.32	60	26	28	1.6	21
3	0.35	60	30	35	3.5	25
4	0.38	60	84	59	6.9	70
5	0.39	60	97	67	21	92
6	0.40	60	100	70.6	24	98

^a Reaction conditions: *ortho*-xylene (0.03 mol), styrene (0.005 mol) and catalyst (0.5 g) at 30 °C. ^b GC yield is shown.

Table 4 Effects of different temperatures on the reaction^a

Entry	Temperature (°C)	Conversion (%)	Selectivity (%)		Yield ^b (%)
			PXE	BPXE	
1	10	15	14	0.6	12
2	30	97	67	21	92
3	50	99	69	28	96
4	70	100	69	30	98.3
5	90	100	69	30	98.6
6	100	100	69	30	99

^a Reaction conditions: *ortho*-xylene (0.03 mol), styrene (0.005 mol) and $\text{AlCl}_3/[\text{Bmim}][\text{Br}]$ (0.5 g, mole ratio: 0.40) at the indicated temperature for 60 minutes. ^b GC yield is shown.

increased with temperature, which do not vary when the temperature is 60 °C.

3.5 Effects of different reaction times on the reaction

When the amount of *ortho*-xylene and styrene is 0.03 and 0.005 mol, respectively, and the mole fraction of $\text{AlCl}_3/[\text{BMIM}][\text{Br}]$ is 0.40%, the reactions are carried out at 70 °C, and the effects of different reaction times on the reaction are shown in Table 5. It can be seen that the percentage conversion of *ortho*-xylene increased with reaction time, and when the reaction time is longer than 60 minutes, the percentage conversion of *ortho*-xylene attained is 100%. Consequently, according to the above results, the synthesis conditions for obtaining 1-phenyl-1-*ortho*-xylene ethane are that the amounts of *ortho*-xylene and styrene

Table 5 Effects of different reaction times on the reaction^a

Entry	Reaction time (min)	Conversion (%)	Selectivity (%)		Yield ^b (%)
			PXE	BPXE	
1	10	18	15	1.8	15
2	30	97	67	21	92
3	60	100	69	28	97.5
4	90	100	69	30	98.6
5	100	100	69	30	99

^a Reaction conditions: *ortho*-xylene (0.03 mol), styrene (0.005 mol) and $\text{AlCl}_3/[\text{Bmim}][\text{Br}]$ (0.5 g, mole ratio: 0.40) at 70 °C. ^b GC yield is shown.

are 0.03 and 0.005 mol, respectively, the mole fraction of $\text{AlCl}_3/[\text{BMIM}][\text{Br}]$ is 0.40%, the reaction time is 60 minutes and the reactions are carried out at 70 °C.

3.6 Reaction mechanism

3.6.1 Mechanism of the reaction. Quantum chemical calculations are a useful tool to predict the reaction mechanisms and kinetics of the alkylation reaction. Styrene (R1) and *ortho*-xylene (R2) have been fully optimized at the B3LYP/6-311++G(d, p) level, the geometrical parameters involving various species of R1, R2, IM, TS and P are shown in Fig. 1 and S2 (ESI[†]), and the important geometrical parameters are given in Table 6. It can be seen that styrene has a Π_8^8 conjugated structure; for R, the bonds of C1–C2 and C2–C3 are averaged which are 1.390 and 1.486 (Å), respectively. When an Al^{3+} ion is combined with a C3 atom in styrene, the length of C3– Al^{3+} is 2.101 (Å), and the obtained IM joined with *ortho*-xylene. This illustrates that the Al^{3+} ion plays an important role in the alkylation processes of styrene and *ortho*-xylene. From IRC calculations for the transition state (TS), we obtain two desired minima states of the process. This indicates a transition state, and it has an imaginary frequency (-182.63 cm^{-1}), the geometrical parameters of the TS are shown in Fig. 1. In the TS,

Fig. 1 Geometrical parameters of the TS.

Table 6 Important geometrical parameters of the R, IM, TS and P ($\text{\AA}$)

Bond length	Reactant	Intermediate	Transition state	Product
C1–C2	1.390	1.395	1.473	1.553
C2–C3	1.486	1.460	1.460	1.576
C2–H4	1.090	1.098	1.097	1.091
C3–H5	1.100	1.100	1.097	1.091
C3–H6	1.081	1.087	1.088	1.097
C7–H8	1.087	1.087	1.086	1.110
C3–Al9		2.101	2.101	1.965
C2–C7			2.319	1.600
C2–H8			2.585	
C7–H4			2.562	
C10–A9				2.054

a C2–H4–C7–H8 four-membered ring is formed, the distances of the bonds are 1.097, 2.562, 1.086 and 2.585 ($\text{\AA}$), respectively, which provides helpful information on the formation of the C2–C7 bond. The bond lengths of C1–C2, C2–C3 and C2–C7 are 1.553, 1.576 and 1.600 ($\text{\AA}$), respectively, which indicates that those bonds are stretched by steric effects of two benzene rings.

The potential energy surface (PES) profile is depicted in Fig. 2. The energy of the IM is lower than that of the reactant by 5.65 kcal mol^{−1}, we can also find that the energy of the P is higher than that of the IM by 15.69 kcal mol^{−1}. This result indicates that the IM is more stable than the P. The energy of the TS is 22.59 kcal mol^{−1}, and this indicates that the activation energy of the alkylation reaction is 28.24 kcal mol^{−1}. This illustrates that the reaction occurs easily, which is in agreement with the experimental results.

3.6.2 Vibrational frequencies. Table 7 lists the main vibration variations of styrene, styrene + *ortho*-xylene + AlCl₃ + [BMIM][Br] and PXE as well as the IR intensity observed in FT-IR spectra; the corresponding infrared spectra are shown in Fig. S3–S5.† It can be seen that the infrared peak appearing at 1710.33 cm^{−1} is assigned to the symmetrical stretching

vibration of (C2–C3) in styrene. When AlCl₃ in [BMIM][Br] is added to styrene and *ortho*-xylene, the symmetrical stretching vibration of (C2–C3) in styrene is red shifted from 1710.33 cm^{−1} to 1106.60 cm^{−1}, which illustrates that the Al³⁺ ion combines with the C3 atom and decreases the C2–C3 bond strength. The infrared peaks 3165.10 and 3247.26 cm^{−1} are attributed to $\nu_s(\text{H5–C3–H6})$ and $\nu_{as}(\text{H4–C3–H5})$, respectively, which are also red shifted to 3026.38 and 3067.59 cm^{−1}, the corresponding vibrational modes are $\nu_s(\text{H4–C3Al–H5})$ and $\nu_{as}(\text{H4–C3Al–H5})$, respectively. This indicates that the Al³⁺ ion joins to form a C3–Al³⁺ bond, which weakens the C3–H4 and C4–H5 bonds. In the product (PXE) the infrared vibrational frequencies 3045.83 and 3119.25 cm^{−1} correspond to the vibrational modes $\nu_s(\text{H5–C3H7–H6})$ and $\nu_{as}(\text{H5–C3H7–H6})$, respectively, and the blue shifts of these vibrational frequencies illustrate that Al³⁺ has been substituted for H7. The infrared peak at 991.48 cm^{−1} is the symmetrical stretching vibration of (C2–C3), which may be due to further weakening caused by product formation. The appearance of the vibrational frequency at 3053.79 cm^{−1}, assigned to the symmetrical stretching vibration of (C2–C7), demonstrates a new bond formation between styrene and *ortho*-xylene.

3.7 Repeated use of the catalyst

When the amount of *ortho*-xylene and styrene is 0.03 and 0.005 mol, respectively, and the mole fraction of AlCl₃/[Bmim][Br] is 0.40%, the reactions are carried out at 70 °C with a reaction time of 1.5 hours. After the reaction, the supernatant liquid is poured out. In order to remove *ortho*-xylene and volatile organic compounds from the ionic liquid, the reaction vessel was put under vacuum, and then the weight of the raw materials was added. The results are listed in Table 8. It can be seen that the ionic liquid can still catalyze the reaction and the percentage yield of PXE is larger than 91% after 6 runs. The activity of the catalyst decreased gradually after 6 runs.

Fig. 2 Energy profiles of the R, IM, TS and P.

Table 7 Main vibration spectrum variations of styrene, *ortho*-xylene, styrene + *ortho*-xylene + AlCl₃ + [BMIM][Br] and PXE

Species	Vibrational mode assignment	Frequency (cm ⁻¹)	IR intensity
Styrene	$\nu_s(\text{C2-C3})$	1710	9.16
	$\nu_s(\text{H4-C2})$	3146	16.20
	$\nu_s(\text{H5-C3-H6})$	3165	2.99
	$\nu_{as}(\text{H4-C3-H5})$	3247	14.99
	$\nu_s(\text{C7-H8})$	3077	27.10
<i>ortho</i> -Xylene	$\nu_s(\text{C2-C3})$	1106	12.33
Styrene + <i>ortho</i> -xylene + AlCl ₃ + [BMIM][Br]	$\nu_s(\text{H4-C3Al-H5})$	3026	26.90
	$\nu_{as}(\text{H4-C3Al-H5})$	3067	2.28
	$\nu_s(\text{C7-H8})$	3161	9.30
	$\nu_s(\text{H4-C2})$	3190	7.86
	$\nu_s(\text{C2-C3})$	991	0.50
	$\nu_s(\text{C2-C7})$	1084	10.36
	$\nu_s(\text{H5-C3H7-H6})$	3045	23.83
	$\nu_s(\text{H4-C2})$	3053	15.26
PXE	$\nu_{as}(\text{H5-C3H7-H6})$	3119	29.02

Table 8 Catalyst performance in ionic liquid for repeated operations

Run	Percentage conversion (%)	Selectivity (%)		Yield (%)
		PXE	BPXE	
1	98.5	69.7	28.3	92.8
2	98.4	69.2	28.3	93.2
3	98.2	69.1	28.0	92.4
4	97.8	68.5	27.5	91.8
5	97.5	68.3	27.4	91.8
6	96.6	67.9	26.8	91.1
7	72.3	47.7	20.5	62.0

According to Table 8, the activity of the catalyst began to decrease after 3–4 cycles. The main explanations for this are leaching of AlCl₃ from the binary mixture and catalyst poisoning by the reaction products and cokes. Measures can be taken to improve the catalytic activity, such as vacuum dehydration, solvent rinsing and the addition of AlCl₃. Besides this, further study has been carried out by our group aiming to improve the catalytic efficiency.

4. Conclusions

In conclusion, green synthesis of 1-phenyl-1-*ortho*-xylene ethane in IL and the reaction mechanism are studied. The effects of different catalysts on the reaction are considered, when the amount of AlCl₃ in IL, *ortho*-xylene and styrene are 0.35, 0.03 and 0.005 mol, respectively, the reactions are performed at 30 °C, and the order of the yield is AlCl₃/[Bmim][Br] (99%) > AlCl₃/[Bmim][Cl] (73%) > H₂SO₄ (56%). The effects of different mole fractions of AlCl₃/[Bmim][Br] on the reaction are investigated; results show that as long as the mole fraction concentration of AlCl₃/[Bmim][Br] is more than 0.40%, the reaction will be able to achieve 100% conversion. The effects of different temperatures on the reaction are studied; the percentage conversion of *ortho*-xylene was increased with the increase of temperature. When the temperature is higher than 60 °C, the

percentage conversion of *ortho*-xylene attained is 100%. The effects of different reaction times on the reaction are investigated; when the reaction time is longer than 60 minutes, the percentage conversion of *ortho*-xylene attained is 100%. The mechanism of the reaction is discussed by quantum chemical calculations and vibrational frequencies are observed in FT-IR spectra. In addition, the repeated use of the catalyst is considered, the ionic liquid can still catalyze the reaction and the percentage yield of PXE is larger than 91% after 6 runs. The activity of the catalyst decreased gradually after 6 runs. The activity of the catalyst can be improved by vacuum dehydration, solvent rinsing and the addition of anhydrous AlCl₃, which is being studied.

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