



## The Catalytic Investigation of Supported Imidazolium-chloroaluminate ( $\text{AlCl}_3$ -ILs) in Friedel-Craft Acylation of Anisole

Thiti Junpirom\*, Praput Thavornytikarn and Puttinan Meepowpan

Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200 Thailand.

\* Author for correspondence; e-mail: Thiti.j@cmu.ac.th

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### ABSTRACT

Two  $\text{AlCl}_3$  supported imidazolium salts (**1**, **2**) were prepared and utilized as the catalysts for the acylation of anisole. The standard conditions for the reaction were optimized. The acylation of anisole using those  $\text{AlCl}_3$  supported imidazolium provided the desired product in high percentage yield in a short period of time. The results revealed that  $\text{AlCl}_3$  supported imidazolium salts are suitable for this reaction when the molar ratio of  $\text{AlCl}_3$ : imidazolium is 2:1 and the reaction smoothly proceeded even at the low temperature such as 0 °C. Moreover, the  $\text{AlCl}_3$ -supported catalyst **1** demonstrated the promising reusability after being catalytically used for 3 times without losing properties.

**Keywords:** imidazolium- $\text{AlCl}_3$ ,  $\text{AlCl}_3$ -supported, mobilized- $\text{AlCl}_3$ , supported ionic liquids, chloroaluminate-ionic liquids

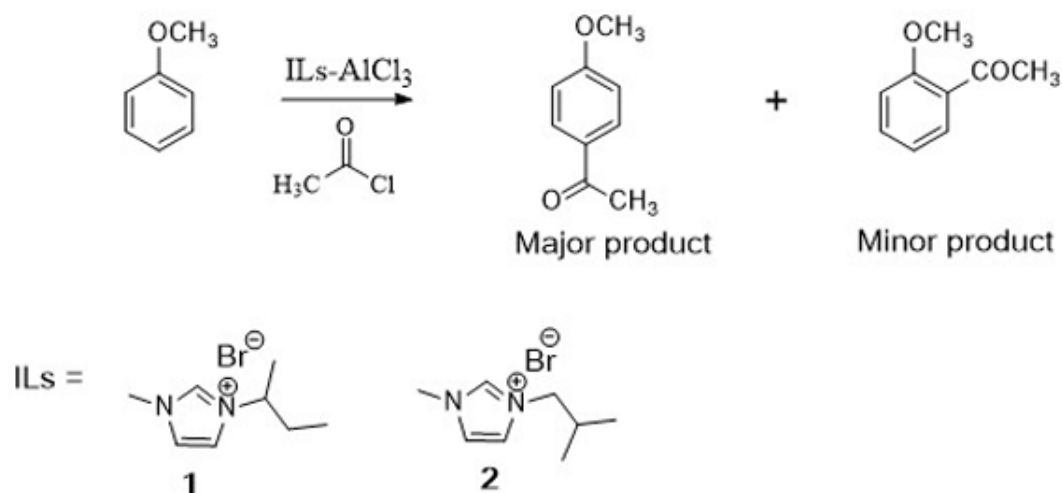
### 1. INTRODUCTION

Fundamentally, Friedel-Craft acylations are performed in the presence of any Lewis acid to promote the acylation of the aromatic rings. The choices of Lewis acid for this reaction is extremely critical to the success of process. Normally, aluminum trichloride ( $\text{AlCl}_3$ ) has been considered as one of the most convenient catalysts because of its commercial availability and highest reactivity compared to the other catalysts such as  $\text{FeCl}_3$ . However, it has been known that the excess amount of  $\text{AlCl}_3$  is usually required to accomplish the complete conversion. Moreover,  $\text{AlCl}_3$  cannot be reused or recovered after the reaction, posing the seriously environmental threat

and generating a severe waste concern on the industrial scale. Therefore, it is quite challenging to reestablish the method for using this catalyst, or replace it with more environmentally benign and rescuable catalysts. Imidazolium salt derivatives or ionic liquids (ILs) have been widely recognized as potential green solvent [1]. In the past two decades, the application of ionic liquids as supporters and catalyst has been intensively studied especially imidazolium-based ILs [2-4]. The initiated work of Seddon and coworker unraveled the interesting properties of imidazolium salts cooperating with several Lewis acids as catalytic-supporters [5].

The properties of Lewis acids such as  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ , and  $\text{AlCl}_3$  have been investigated on supporting imidazolium salts, which were considered to possess the same catalytic properties but exhibit more environmental friendliness and reusability [6, 7]. In this

research, we introduce another interesting function of imidazolium salts (**1**, **2**) to support the well-established catalyst chloroaluminate ( $\text{AlCl}_3$ ) in the acylation of anisole, which has been established as the most common catalyst on Friedel-Craft acylations.



**Figure 1.** The acylation of anisole using  $\text{ILs-AlCl}_3$  as catalyst [1-(*sec*-Butyl)-3-methyl-imidazolium bromide (**1**), 1-(*iso*-butyl)-3-methyl-imidazolium bromide (**2**)].

## 2. MATERIALS AND METHODS

### 2.1 Materials

Dichloromethane and toluene were distilled and stored over molecular sieves in tightly sealed containers to prevent the exposure to oxygen in the air. Anhydrous  $\text{AlCl}_3$  was purchased from Aldrich, opened in a glove box ( $\text{N}_2$ ) and stored in a desiccator. 1-Methyl imidazole, *iso*-butylbromide, and *sec*-butylbromide were purchased from Sigma-Aldrich as AR grade reagent and used without further purification. All experiments involving the preparation of ionic liquids, the catalytic and recovered processes were performed under inert atmosphere ( $\text{N}_2$ ) to ensure the moisture-free reaction conditions.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer (400 MHz). The chemical shifts ( $\delta$ ) are reported in part-per-million (ppm) relative to tetramethylsilane

( $\text{Me}_4\text{Si}$ ) as the internal standard (0.0 ppm) or (for  $^1\text{H}$  NMR spectra) proton resonance resulting from incomplete deuteration of the NMR solvent. FT-IR spectra were obtained from a Bruker Tensor 27 spectrophotometer. All melting points were obtained from electrothermal melting point apparatus and uncorrected.

### 2.2 Experimental and Procedure

#### 2.2.1 Synthesis of 1-alkyl-3-methylimidazolium derivatives [1, 2]

In a round bottom flask equipped with a reflux condenser, 1-methylimidazole 1.0 (eq.) and appropriate alkyl halide (1.1 eq.) were mixed together in toluene (1 mL *N*-methylimidazole / 1 mL toluene) under nitrogen atmosphere. The stirred solution was heated to 80 °C for 48 hour. After the reaction mixture was cooled to room temperature,

all solvent was evaporated to dryness under reduced pressure affording dark yellow liquids. To completely remove the residual solvent, the crude product was further stirred under high vacuum (0.001 torr) at 80 °C for another 24 hours produced the viscous dark yellow liquid (**1**) or white amorphous solid (**2**), dec. 330-337 °C.

1-(*sec*-Butyl)-3-methyl-imidazolium bromide (**1**), viscous dark yellow liquid (77%) IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3143, 3089, 1630, 1570, 1461, 1426.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm,  $J/\text{Hz}$ ): 0.90 (3H, t,  $J = 7.25$  Hz), 1.61 (3H, d,  $J = 7.25$  Hz), 4.14 (1H, s), 1.84-1.97 (1H, m), 4.59-4.64 (1H, m), 7.26 (1H, s), 7.36, (1H, s), 7.49 (1H, s).

1-(*iso*-butyl)-3-methyl-imidazolium bromide (**2**), 330-337 °C (dec.) (84%) IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3448, 2963, 2053, 1637, 1561, 1473, 1166, 753.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm,  $J/\text{Hz}$ ): 0.86-0.87 (6H, d,  $J = 4.8$  Hz) 2.07-2.17 (1H, m), 4.16 (1H, s), 4.04 (3H, s), 4.03-4.06 (2H, m), 7.45 (1H, s), 7.63 (1H, s), 10.09 (1H, s).  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ,  $\delta$ , ppm,  $J/\text{Hz}$ ): 1.00-1.01 (6H, d,  $J = 6.7$  Hz). 2.07-2.10 (1H, dt,  $J = 2.2$  Hz), 4.13 (3H, s), 4.24-4.26 (2H, d,  $J = 7.29$  Hz), 7.79 (1H, s), 7.80 (1H, s), 9.09 (1H, s).

### 2.2.2 Preparation of the supported $\text{AlCl}_3$ -ILs(**1**, **2**)

The supported  $\text{AlCl}_3$  imidazolium salts were prepared by dissolving **1** or **2** in dry  $\text{CH}_2\text{Cl}_2$  (1 g /1 mL) then  $\text{AlCl}_3$  was slowly added in portions into the solution under  $\text{N}_2$  atmosphere at 0 °C. This resulting solution was allowed to room temperature and continuously stirred for 18 hour to obtain the homogeneity of  $\text{AlCl}_3$ -ILs. After that period, all volatile compounds were carefully evaporated on a rotary evaporator under nitrogen. The supported adduct was further dried at 1 Torr for 2 hours to yield  $\text{AlCl}_3$ -**1** as pale-red viscous liquid or  $\text{AlCl}_3$ -**2** as white

powder. The catalyst was weighed in a glove box and stored in a desiccator to avoid the moisture and air exposure. The molar ratio of  $\text{AlCl}_3$  defined as

$$X(\text{AlCl}_3) = n(\text{AlCl}_3)/(n(\text{AlCl}_3)+n(\text{ILs}))$$

[1-(*sec*-butyl)-3-methyl-imidazolium]-chloroaluminate, ( $\text{AlCl}_3$ -**1**) IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3089, 2418, 1640, 1563, 1458.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm,  $J/\text{Hz}$ ): 0.92 (3H, t,  $J = 8.25$  Hz), 1.62 (3H, d,  $J = 8.25$  Hz), 1.84-1.97 (2H, m), 4.16 (1H, s), 2.29 (2H, m), 4.59-4.67 (1H, m), 7.56 (1H, s), 7.70 (1H, s), 10.34 (1H, s).

[1-(*iso*-butyl)-3-methyl-imidazolium]-chloroaluminate, ( $\text{AlCl}_3$ -**2**) IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3065, 2363, 1640, 1164, 840, 599. No satisfied NMR data was obtained due to the poor solubility of  $\text{AlCl}_3$ -**2**.

## 2.3 Acylation of Anisole and the Recovery and Reused of Prepared Catalysts

### 2.3.1 Acylation of anisole using ILs as solvent

In a reaction flask equipped with a magnetic bar, a gas inlet, and a septum,  $\text{AlCl}_3$  (3.0 eq) was dissolved in ILs **1** (20.0 eq.) and anisole (1.0 eq.) were mixed together and cooled in an ice bath. Then, acetyl chloride (2.0 eq.) was slowly added dropwise to the mixture. The reaction was continuously stirred at 0 °C.

After 20 minutes, the reaction was quenched with 10% HCl and allowed to cool to room temperature. The mixture was extract several times with dry  $\text{Et}_2\text{O}$  then filtered through a pack of silica gel and subsequently washed 2 times with DI water, brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The acylation product was obtained without further purification after all volatile organic compounds were evaporated and dried in vacuo. The conversion (%) and selectivity of *p*-acetyl anisole (major product) to

*o*-acetyl anisole (minor product) was obtained through the  $^1\text{H}$  NMR (400 MHz) analysis.

### 2.3.2 Acylation of anisole using ILs as supported catalyst

In a reaction flask equipped with a magnetic bar, a gas inlet, and a septum, a selected  $\text{AlCl}_3$ -supported imidazolium salt ( $\text{AlCl}_3$ -ILs) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  under  $\text{N}_2$ . The concentration was adjusted to 1 M. In another reaction flask, anisole (1.0 eq.) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (1g/1mL) and then subsequently cooled in an ice bath. The completely dissolved  $\text{AlCl}_3$ -ILs and acetyl chloride (2.0 eq.) were transferred to the flask containing anisole through a teflon tube at  $0^\circ\text{C}$ . Next, the reaction was continuously stirred at  $0^\circ\text{C}$  for 20 minutes.

After the reaction was complete, the reaction mixture was allowed to cool to room temperature and diethyl ether ( $\text{Et}_2\text{O}$ ) was then added to dissolve all organic compounds. The mixture was cooled to  $0^\circ\text{C}$  (ice-water) and maintained for another 30 minutes. Two phases were observed during this period as  $\text{AlCl}_3$ -IL gradually settled down as the more condensed phase, the upper organic layer was carefully decanted. The remaining viscous liquid was washed several times with  $\text{Et}_2\text{O}$  to remove all organic residues. All combined organic phases were filtered through a pack of silica gel and subsequently washed 2 times with DI water, brine and dried over anhydrous  $\text{Na}_2\text{S}_2\text{O}_4$ . The acylation product was obtained without further purification after all volatile organic compounds were evaporated and dried *in vacuo*. The conversion (%) and selectivity to main product (*p*-acetyl anisole) was obtained through the  $^1\text{H}$  NMR (400 MHz) analysis.

### 2.3.3 Method for recovery and reused of supported catalysts

To reuse  $\text{AlCl}_3$ -ILs, the lower viscous layer was evaporated to dryness under  $\text{N}_2$ , then further dried under high vacuum for another 1 hour. The recovered catalyst was stored in a desiccator since the presence of moisture could affect the reactivity of Lewis acid catalysts and hence posed the great impact on the efficiency of the  $\text{AlCl}_3$ -ILs. It is necessary to carefully perform the reaction under inert atmosphere using extremely dry glassware. This is primarily attributed to the formation of super acids ( $\text{AlCl}_3\text{H}^+$ ) which could seriously interrupt the activity of  $\text{AlCl}_3$  and hence no acylation reaction is observed [8].

## 3. RESULTS AND DISCUSSION

### 3.1 The Efficiency of $\text{AlCl}_3$ -ILs (1)/ $\text{CH}_2\text{Cl}_2$ and $\text{AlCl}_3$ /ILs (1) Compared to $\text{AlCl}_3$ / $\text{CH}_2\text{Cl}_2$ on Acylation Reaction of Anisole

The yields and the selectivity of the acylation of anisole with standard condition ( $\text{AlCl}_3$ / $\text{CH}_2\text{Cl}_2$ ) compared to  $\text{AlCl}_3$ /ILs (1) are list in **Table 1** (entry 1 and 2). When the solvent was changed from  $\text{CH}_2\text{Cl}_2$  to ILs (1) the conversion (%) of this reaction had significantly decreased. We suggested that the imidazolium **1** salt remained in a state of viscous glassy material at  $0^\circ\text{C}$  which would reduce the activity of the  $\text{AlCl}_3$  and ionic liquid itself. On the other hand, when ILs (1) was introduced in to the reaction as supported-catalyst  $\text{AlCl}_3$ -ILs (1)/ $\text{CH}_2\text{Cl}_2$ , the reaction proceeded smoothly at  $0^\circ\text{C}$  with better conversion and selectivity (**Table 1**, entry 6)

### 3.2 The Effect of Molar Fraction of $\text{AlCl}_3$ : ILs (1, 2) on the Acylation Reaction of Anisole

The molar fraction of  $\text{AlCl}_3$ :imidazolium salts (1) were varied to explore the most suitable condition for anisole acylation (**Table 1**). The yield and selectivity of acylation

of anisole were gradually maximized and then decreased when the molar fraction increased. The maximum value of 88 % yield, and 98.2 % selectivity was obtained when the molar ratio of  $\text{AlCl}_3$  to **3** was 0.67. On the other hand, when the molar fraction reached 0.75, the % conversion was no longer improved but the selectivity of the main product slightly decreased. This allowed us to conclude that the molar ratio of 2:1 (molar fraction 0.67) was the best condition for acylation of anisole [9]. The excess amount of  $\text{AlCl}_3$  when increasing the molar ratio of  $\text{AlCl}_3$  could lead to the formation of other undesired species such as  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$  to

$\text{Al}_3\text{C}_{10}^-$ , in ILs (**1**, **2**), slightly reducing the catalytic ability of the prepared catalysts. Therefore, these catalysts were mainly basic when the molar ratio less than 0.67, whereas when the ratio was over 0.67, the catalysts would be acidic. For the reason, we suggested that  $\text{AlCl}_3$  could serve as a catalyst on the acylation of anisole with its molar fraction to imidazolium salt **1** was 0.67. On the contrary, imidazolium salt **2** is an amorphous solid at room temperature and sparingly dissolve or form homogeneous adduct with  $\text{AlCl}_3$ . Thus, it implies that imidazolium salt **2** might not be an appropriate  $\text{AlCl}_3$  supported-ILs like its analogous compound **1**.

**Table 1.** Effect of the molar fraction of  $\text{AlCl}_3$ -ILs (**1**, **2**) on the conversion and the selectivity to main product on acylation of anisole with  $n[\text{AlCl}_3\text{-1, 2} : n[\text{anisole}] = 1.5:1$ ,  $n(\text{anisole}) : n(\text{acetyl chloride}) = 1:2$ ,  $0^\circ\text{C}$  for 20 min.

| Catalyst              | $\text{AlCl}_3$ ; 1,<br>or 2 | Molar fraction,<br>X ( $\text{AlCl}_3$ ) | Yield (%) <sup>c</sup> | Major product<br>selectivity (%) <sup>c</sup> |
|-----------------------|------------------------------|--|------------------------|---|
| - <sup>a</sup>        | -                            | -  | 85                     | 90.7  |
| <b>1</b> <sup>b</sup> | -                            | -  | 34                     | 90.4  |
| 1                     | 1.0:0.5                      | 0.33                                     | 0                      | 0   |
| 1                     | 1.0:1.0                      | 0.50                                     | 8                      | 98.0  |
| 1                     | 1.5:1.0                      | 0.60                                     | 48                     | 98.6  |
| 1                     | 2.0:1.0                      | 0.67                                     | 88                     | 98.2  |
| 1                     | 2.5:1.0                      | 0.71                                     | 80                     | 96.4  |
| 1                     | 3.0:1.0                      | 0.75                                     | 77                     | 89.7  |
| 2                     | 1.0:1.0                      | 0.50                                     | 0                      | 0   |
| 2                     | 2.0:1.0                      | 0.67                                     | 27                     | 80.2  |
| 2                     | 2.5:1.0                      | 0.71                                     | 34                     | 84.4  |

<sup>a</sup> The acylation of anisole with  $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$  without ILs at  $0^\circ\text{C}$ , 20 min.; <sup>b</sup> The acylation of anisole with  $\text{AlCl}_3$ /ILs (**1**) at  $0^\circ\text{C}$ , 20 min.; <sup>c</sup> The conversion (%) and selectivity of major product (*para*) was determined by  $^1\text{H}$  NMR 400 MHz.

### 3.3 The Optimization of Molar Ratio on the Acylation Reaction and Its Selectivity

The effect of molar ratio of  $\text{AlCl}_3\text{-1}$  to anisole on the yield and selectivity are summarized in **Table 2**. Although this reaction progressed smoothly at  $0^\circ\text{C}$  more than 1 equivalence of catalyst is still necessary to drive the reaction to completion. The maximum

yield was obtained when the molar ratio of  $\text{AlCl}_3\text{-1}$  was 1.5:1 and significantly decreased when the molar ratio exceeded 2:1. For the selectivity of this reaction, when the molar ratio was higher than 2:1, the selectivity slightly decreased. Therefore, it can be concluded that the ratio of 1.5:1 equivalent of ILs ( $\text{AlCl}_3\text{-1}$ ) was appropriate for the acylation of anisole.

**Table 2.** Optimization of molar ratio of AlCl<sub>3</sub>-ILs (**1**) to anisole on the acylation reaction with n(anisole): n(acetyl chloride) = 1:2, molar fraction of AlCl<sub>3</sub> = 0.67, 0 °C for 20 min.

| AlCl <sub>3</sub> -ILs ( <b>1</b> ): anisole | Conversion (%) <sup>a</sup> | Selectivity (%) <sup>a</sup> |
|--|-----------------------------|------------------------------|
| 0.5:1  | 70                          | 97.2                         |
| 1.0:1.0                                      | 88                          | 98.2                         |
| 1.5: 1.0                                     | 90                          | 98.4                         |
| 2.0:1.0                                      | 87                          | 98.2                         |
| 1.5:1.0                                      | 77                          | 88.0                         |
| 3.0:1.0                                      | 70                          | 84.0                         |

<sup>a</sup> The conversion (%) and selectivity of major product (*para*) was determined by <sup>1</sup>H NMR 400 MHz.

### 3.4 Temperature Effect on the Acylation Reaction

The impact of the reaction temperature on the result of acylation reactions catalyzed by AlCl<sub>3</sub>-**1** was investigated. The percent conversion decreased greatly when the temperature was *ca.* 30 °C (r.t.) On the contrary, the major product selectivity

declined slightly when the temperature of reaction was risen. Since acylation is an exothermic reaction, the equilibrium conversion logically decreases with the higher reaction temperature. Therefore, we suggested that 0-10 °C was the best optimal reaction temperature for this reaction.

**Table 3.** Reusing performance of AlCl<sub>3</sub>-ILs (**1**) with n[AlCl<sub>3</sub>-ILs(**1**), (**2**) : n[anisole] = 1.5:1, n(anisole) : n(acetyl chloride) = 1:2, molar fraction of AlCl<sub>3</sub> = 0.67, at 0 °C for 20 min.

| Reusing time of AlCl <sub>3</sub> -ILs(1) | Conversion (%) <sup>a</sup> | Selectivity (%) <sup>a</sup> |
|---|-----------------------------|------------------------------|
| 1   | 88                          | 98.2                         |
| 2   | 85                          | 98.0                         |
| 3   | 77                          | 96.5                         |
| 4   | 50                          | 97.8                         |
| 5   | 20                          | 88.7                         |

<sup>a</sup> The conversion (%) and selectivity of major product (*para*) was determined by <sup>1</sup>H NMR 400 MHz.

### 3.5 Reusability of AlCl<sub>3</sub>-**1**

The reusability of chloroaluminate on imidazolium salt **1** (AlCl<sub>3</sub>-**1**) was investigated and the related results were summarized in **Table 3**. The catalyst was separated after being used in the acylation and reused for the next experiment under the identical experimental conditions. These data collected from the cycle No.1 to No.3 suggested that

the AlCl<sub>3</sub>-**1** could be reused for 3 times with nearly same activities. However, the data acquired from the cycle No.4 and No.5 exhibited the less activities of catalyst but same selectivity, suggesting the slight deactivation of the ionic liquid **1**. The possible decline of the catalytic ability could stem from the loss of AlCl<sub>3</sub> to the reaction after being used, resulting in a lower activity of



the catalyst [10]. Hence, the  $\text{AlCl}_3$ -**1** should not be reused more than 3 times to maintain its best efficiency. However, the degenerated  $\text{AlCl}_3$ -**1** could be reactivated by adding more  $\text{AlCl}_3$  into the mixture, which could restore the activity of the catalyst. On the other hand, the reusability of  $\text{AlCl}_3$ -**2** could not be thoroughly studied, since this chloroaluminate-imidazolium salt could not be prepared as the homogeneous mixture in most of common organic solvents, all  $\text{AlCl}_3$  was totally lost after the acylation was carried out.

#### 4. CONCLUSION

The optimized parameters for conducting the anisole acylation using  $\text{AlCl}_3$ -**1** and  $\text{AlCl}_3$ -**2** have been studied. The results showed that the following set of parameter afforded the best conversion and selectivity of this reaction:  $n[\text{AlCl}_3\text{-1, 2}] : n[\text{anisole}] = 1.5:1$ ,  $n[\text{anisole}] : n[\text{acetyl chloride}] = 1:2$ , with molar fraction of  $\text{AlCl}_3 = 0.67$ , at  $0^\circ\text{C}$  for 20 minute. The investigation also indicated that imidazolium **1** was a better supporter than imidazolium **2**. The efficiency of  $\text{AlCl}_3$ -**1**, both percent conversion and product selectivity showed no significantly change after being used for 3 times as a catalyst.

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