

Microwave-accelerated Claisen rearrangement in bicyclic imidazolium [b-3C-im][NTf₂] ionic liquid

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Abstract—With microwaves, a chemically stable ionic liquid [b-3C-im][NTf₂] recently developed in our laboratory was used as solvent and successfully applied to accelerate Claisen rearrangement reactions at high temperatures. In the presence of Lewis acid MgCl₂, these thermal rearrangements could be achieved in similar reaction times but at lower temperature. For the microwaved reactions studied in this work, without sacrificing isolated yields, the reaction times were significantly reduced from hours (by conventional heating) to <3 min. Our result also demonstrated that [b-3C-im][NTf₂] ionic liquid was a useful solvent substitute and could be recycled multiple times for the studied rearrangement reaction at elevated temperatures.

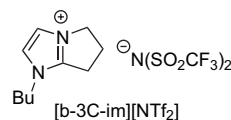
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1. Introduction

Ionic liquids are organic salts that are liquid at low temperatures (<100 °C).¹ The wide liquid range, superior thermal and chemical stabilities, excellent solubility with many organic compounds, and very low vapor pressure have made ionic liquids, in particular room-temperature ionic liquids, attractive as reaction media for organic synthesis. To date, a rich number of chemical reactions have been reported and carried out in ionic liquids. These include, for example, Friedel–Crafts alkylation, Pictet–Spengler condensation, Heck reaction as well as Stille, Negishi, and Trost–Tsuji reactions, Michael addition, olefin metathesis, Diels–Alder cycloaddition, and many others.¹

In our laboratory, we have been interested in developing new room-temperature ionic liquids with specific aims to evaluate them as novel and stable media for chemical and biochemical applications.² As recent examples, we successfully employed 1-butyl-2,3-dimethylimidazolium ([bdmim]) ionic liquids as solvents to achieve total synthesis of small libraries of tetrahydro-β-carbolinediketopiperazines as demethoxyfunitremorgin C analogs and tetrahydro-β-carbolinequinoxalinones.^{2c,d} In our continuous development of new ionic liquids for organic synthesis, we described here the application of a newly developed bicyclic imidazolium-based ionic liquid, [b-3C-im][NTf₂] (1-butyl-2,3-

trimethyleneimidazolium bis(trifluoromethanesulfonyl)imide),^{2a,b} as promising solvent for use in microwave-accelerated Claisen rearrangement of various allyl aryl ethers carried out at high temperatures. Recently, the remarkable chemical stability of ionic liquid has been demonstrated.^{2a,b} In this work, we further investigated its thermal stability and tested its inertness for use as solvent in high-temperature Claisen rearrangements. In literature, there were reports on the microwave-assisted Claisen rearrangements using conventional organic solvent doped with the ionic liquid or the solvent–ionic liquid biphasic system.³ No Claisen rearrangement reactions performed purely in ionic liquids accelerated by microwaves have been reported.



2. Results and discussion

When 200 °C or higher temperatures are required for organic reactions, the choice of solvents is often limited primarily because issues such as safety, environmental, and other considerations dictate the final selection of organic solvents. As one well studied reaction in synthetic organic chemistry, Claisen rearrangement typically requires high temperatures and long reaction hours.⁴ In this work, we envisaged that, in tandem with microwaves, ionic liquids should be the solvent of choice for such high-temperature organic reactions mainly due to their negligible vapor pressure

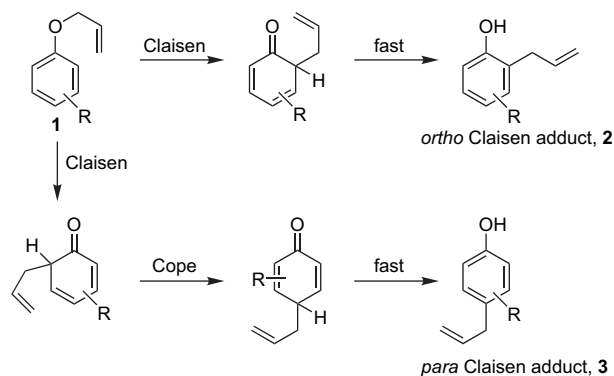
Keywords: Bicyclic imidazolium ionic liquid; Claisen rearrangement; Microwaved reaction.

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and high polarity. Both properties are unique and particularly attractive for high-temperature Claisen rearrangement reactions mediated by microwaves; that is, the minimal vapor pressure safeguards high-temperature experiments carried out in laboratory and high polarity makes the ionic liquid an excellent microwave absorber, ultimately leading to efficient transformation of reactions in short time. As an added benefit, polar solvents are well known in the literature to increase rates of the rearrangement.⁴ This protocol of using microwaves to accelerate Claisen rearrangement in water-immiscible ionic liquids such as [b-3C-im][NTf₂] is advantageous for three reasons: first, high reaction rates can be obtained and, second, the rearranged products may be easily isolated by straightforward ether extraction. Last, the ionic liquid used as solvent can be recovered for reuse if desired. Apart from the aforementioned benefits of replacing organic solvents with ionic liquids, the high solubility power to organic materials by ionic liquids clearly facilitates reaction processes.

Scheme 1 outlines the reaction pathways of Claisen rearrangement.⁴ In the rearrangement of an allyl aryl ether **1**, the thermal [3,3] sigmatropic reaction affords an *ortho*-dienone that readily enolizes into an *ortho*-allylphenol **2** (Scheme 1). When the rearrangement takes place on an *ortho*-position bearing a substituent, a concomitant Cope rearrangement occurs followed by enolization, leading to *para*-allylphenol **3** (Scheme 1). This rearrangement is known to be characteristically irreversible toward the formation of the phenol compounds under thermodynamic control and the corresponding *ortho*-Claisen adduct **2** is usually isolated as the major product.⁴



Scheme 1. Claisen rearrangement of allyl aryl ethers (**1a–j**).

In this study, we aimed at performing high-temperature Claisen rearrangement in a chemically stable and non-volatile [b-3C-im][NTf₂] room-temperature ionic liquid using microwaves with a specific goal to achieve the rearrangement with good-to-high isolated yields and in short reaction time. Among all requisite allyl aryl ethers **1** used in this work, allyl phenyl ether (R=H) and allyl *ortho*- and *para*-tolyl ethers (R=*o*- and *p*-CH₃, respectively) were available commercially (Scheme 1). Others could readily be prepared by the straightforward allyl bromide reaction with the appropriate phenols using potassium carbonate as the base in acetonitrile under reflux condition.⁵ Reaction times required for preparing Claisen substrates **1** were typically 1–3 h and all were obtained with high isolated yields

(82–90 mol %). Yields and spectroscopic properties were in good agreement with literature values.

Experiments of Claisen rearrangement were conducted in [b-3C-im][NTf₂] ionic liquid by microwaves at elevated temperatures. We initially investigated this microwave-assisted reaction at temperatures below 200 °C with the hope that microwaves might more or less facilitate the rearrangement. However, we found that the starting ether **1j** was totally unreactive and no products were observed for microwaved reactions carried out at 150 °C in 20 min and only trace amounts of the desired *ortho*-Claisen adduct **2j** were obtained at 175 °C. Therefore, reactions in [b-3C-im][NTf₂] ionic liquid at 250 °C by microwaves (80 W) were investigated. The results are shown in Table 1. To our delight, all studied reactions were clean and found to finish in 90–150 s, and good-to-high yields (69–82%) of the expected Claisen rearrangement products were attained for all of substituted allyl aryl ethers **1a–j** studied. The reaction times were optimized by monitoring the reaction mixture at different time intervals by TLC. In addition, under our experimental conditions no derivatives of dihydrobenzo[*b*]furan and other side reactions were found in this ionic liquid.⁶

Results of Claisen rearrangement in Table 1 clearly indicated that, despite only short reaction time required by microwaves, electron-donating substituent in phenyl ring increased the reaction rate and therefore facilitated the rearrangement (**1j** vs **1d** and **1g**, for example). Electron-withdrawing groups, however, decreased the reaction rate (Table 1). When the preferential *ortho*-position for rearrangement is not blocked, as with 4-substituted allyl phenyl ethers (**1d**, **1g**, and **1j**), for example, a normal Claisen rearrangement occurs to form 2-allyl-4-substituted phenols (**2d**, **2g**, and **2j**) in good yields (77%, 73%, and 80%, respectively). When one of the preferential *ortho*-positions for allyl group migration is blocked, as with 2-substituted allyl aryl ethers, typically two rearranged products (**2+3**) occur (Table 1). For example, under our experimental condition the ether **1b** readily rearranged to afford the products **2b** and **3b** (49% and 21%, respectively,) with **2b** as the major isolated product. In the case of the ether **1e**, the first is the rearrangement to form 2-allyl-6-methoxyphenol (**2e**) in 64% yield and the second rearranged product is 4-allyl-2-methoxyphenol (**3e**, 18% yield). However, for 1-allyloxy-2-chlorobenzene (**1h**), no *para*-substituted Claisen–Cope adduct **3h** was observed and only the *ortho*-product **2h** from simple Claisen rearrangement was isolated (69%). Moreover, regardless of the nature of substituent in phenyl ring, *meta*-substituted allyl aryl ethers proceeded most slowly in reaction rate (Table 1). These results were all consistent with reports in the literature.⁴ These experimental observations could be rationalized as the rearrangement proceeding through an ion-pair mechanism, where the allyl group ionized as an anion and the aromatic moiety as a cation.⁴

Though microwaves significantly speeded up the reaction of Claisen rearrangement and furnished the synthesis of allylphenols in short reaction time,⁷ we, however, decided to investigate further the incorporation of ancillary agents to achieve the rearrangement in similar reaction time but with lower temperatures. Since Lewis acids have been

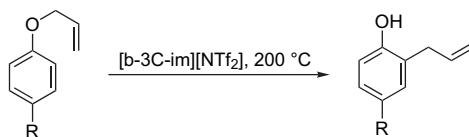
Table 1. Microwave-accelerated Claisen rearrangement of allyl aryl ethers (**1a–j**) in [b-3C-im][NTf₂] ionic liquid at 250 °C

Reaction scheme showing the Claisen rearrangement of allyl aryl ether **1** (with substituent R) to products **2** and **3** using [b-3C-im][NTf₂] ionic liquid under microwave irradiation at 250 °C.

Entry	Starting 1	Products (2+3)	Reaction time (s)	Isolated yield (%)
1	(1a)		90	75
2	(1b)	+ (2.4 : 1)	90	70
3	(1c)	+ (1.2 : 1)	120	74
4	(1d)		90	77
5	(1e)	+ (3.5 : 1)	90	82
6	(1f)	+ (3.5 : 1)	120	71
7	(1g)		90	73
8	(1h)		120	69
9	(1i)	+ (1 : 1.4)	150	71
10	(1j)		120	80

known in the literature to facilitate the rate of Claisen rearrangements,⁴ we accordingly employed anhydrous magnesium chloride used as an inexpensive Lewis acid to carry out Claisen rearrangement at lower temperatures. After several trials of these MgCl₂-promoted and microwave-accelerated rearrangement experiments, we were pleased to find that the inclusion of 1 molar equiv magnesium chloride in [b-3C-im][NTf₂] ionic liquid solution was able to furnish

rearrangements of allyl aryl ethers at lower than 200 °C with reaction rates similar to those obtained at 250 °C. Thus, 4-substituted allyl phenyl ethers (**1a**, **1d**, **1g**, and **1j**) achieved the rearrangement in 150–180 s with high isolated yields (75–82%) into the corresponding *ortho*-Claisen adducts (**2a**, **2d**, **2g**, and **2j**) (Table 2). As a representative example used for rate comparison, allyl phenyl ether (**1a**) rearranged to 2-allylphenol (**2a**) in 150 s with magnesium

Table 2. Lewis acid-promoted, microwave-accelerated Claisen rearrangement of allyl aryl ethers (**1a**, **1d**, **1g**, and **1j**) in [b-3C-im][NTf₂] ionic liquid at 200 °C

Entry	R	Conventional heating		Microwave heating			
		Without MgCl ₂		Without MgCl ₂		With MgCl ₂	
		Reaction time (h)	Isolated yield (%)	Reaction time (min)	Isolated yield (%)	Reaction time (s)	Isolated yield (%)
1	H (1a)	2	65	15	74	150	79
2	CH ₃ (1d)	3.5	71	12	79	150	75
3	CH ₃ O (1g)	2.5	74	9	78	150	82
4	Cl (1j)	4	79	17	70	180	76

chloride in [b-3C-im][NTf₂] ionic liquid at 200 °C, compared to 15 min without magnesium chloride and 2 h in total with conventional heating (Table 2, entry 1). Among the compounds tested, as expected, electron-withdrawing substituent in the starting ether (**1j**) required the longest reaction time to furnish the rearrangement (Table 2, entry 4). Under our experimental condition, all Claisen rearrangement reactions proceeded cleanly and side reactions were not observed. The results clearly demonstrated that, in combination with Lewis acid, microwave heating effectively accelerated rearrangement reaction and therefore afforded higher conversion in short reaction time at elevated temperature.

Since thermal Claisen rearrangement reactions carried out at high temperatures required ionic liquid solvents with higher thermal stability, we accordingly conducted the stability as well as the potential reuse of [b-3C-im][NTf₂] under microwave irradiation at elevated temperatures. Using allyl 4-tolyl ether (**1d**) as the Claisen substrate for the rearrangement reaction performed at high temperature (250 °C), as expected, the desired 2-allyl-4-methylphenol (**2d**) was conveniently isolated as the sole product with good yield (74%) (Fig. 1A, cycle 1). It was observed, however, that the reaction mixture was darkened somewhat after exposure to 250 °C with microwaves. Though a change in color was associated with [b-3C-im][NTf₂], this ionic liquid nevertheless could be reused for the rearrangement reaction in a total of three cycles without drastically sacrificing yields (74%, 79%, and 77% for cycles 1, 2, and 3, respectively) (Fig. 1A, cycles 1–3). After being reused two times, yields of the Claisen rearrangement in [b-3C-im][NTf₂] for the next two cycles decreased significantly (59% and 56%) (Fig. 1A, cycles 4 and 5) and, therefore, the used ionic liquid was subjected to regeneration using activated charcoal in hot methanol (for details, see Section 4). As shown in Figure 1A, the regenerated [b-3C-im][NTf₂] ionic liquid could again be used as solvent for the sixth and seventh cycles of rearrangement reaction and no apparent loss of isolated yields of the product **2d** was observed for the reactions performed at 250 °C (79% and 71% for cycles 6 and 7, respectively). As also shown in Figure 1B, for the MgCl₂-promoted rearrangement of the ether **1d** carried out at 200 °C by microwaves (80 W), the [b-3C-im][NTf₂] ionic liquid could be readily recycled six times with consistent isolated yields (70–81%). We noted that, under the experimental condition, slightly higher yield was obtained as the rearrangement reaction carried out in the regenerated ionic liquid than in the

ionic liquid recovered from the reaction but prior to regeneration (for example, 77% vs 73% for cycles 1 and 2). For the study shown in Figure 1B, the ionic liquid was regenerated and then reused after every two cycles. If [b-3C-im][NTf₂] ionic liquid was regenerated right after every cycle of

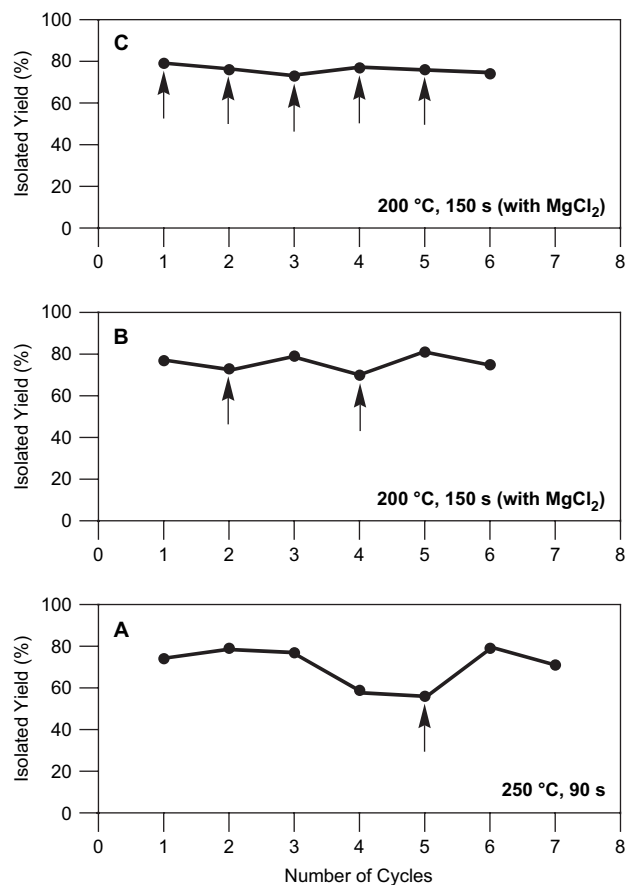


Figure 1. Reuse of [b-3C-im][NTf₂] ionic liquid for microwaved Claisen rearrangement of: (A) allyl 4-tolyl ether **1d** at 250 °C, (B) allyl 4-tolyl ether **1d** with MgCl₂ at 200 °C, and (C) allyl phenyl ether **1a** with MgCl₂ at 200 °C. For Claisen rearrangement performed at 250 °C (A), the [b-3C-im][NTf₂] ionic liquid was regenerated after five reaction cycles and then used directly for the sixth and seventh cycles. For MgCl₂-promoted Claisen rearrangement carried out at 200 °C, [b-3C-im][NTf₂] ionic liquid was regenerated after every two cycles (B) or on each reaction cycle (C). Average isolated yield of Claisen adduct was 71±10% for (A), 76±4% for (B), and 76±2% for (C), respectively. In the figure, arrow indicated the point of ionic liquid regeneration and reuse. For details in ionic liquid regeneration, see Section 4.

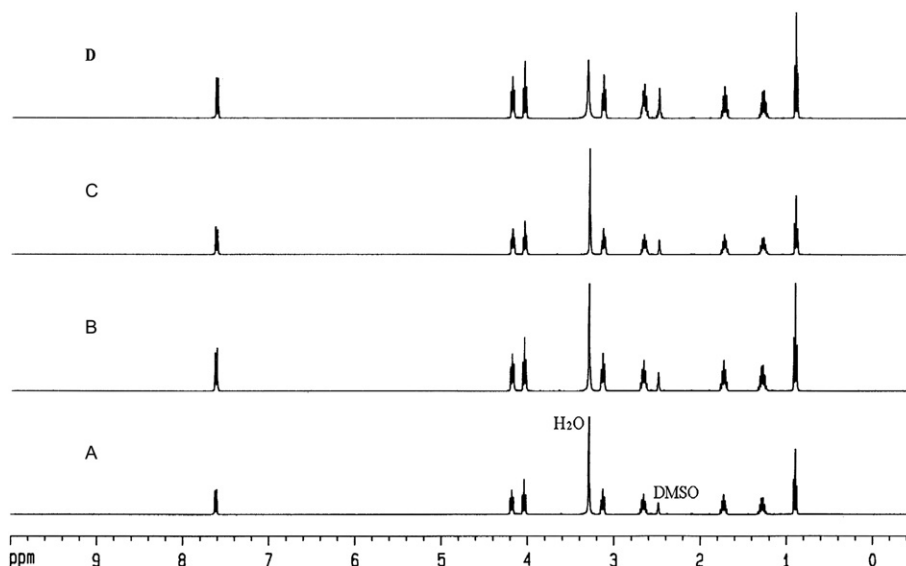


Figure 2. Proton NMR spectra of: (A) [b-3C-im][NTf₂] ionic liquid alone (pale yellow color), (B) [b-3C-im][NTf₂] previously heated by microwaves at 200 °C for 150 s (very light brown color), (C) [b-3C-im][NTf₂] ionic liquid recovered from the Claisen rearrangement of allyl phenyl ether **1a** in the presence of MgCl₂ with heating by microwaves at 200 °C for 150 s (dark brown color), and (D) the regenerated [b-3C-im][NTf₂] ionic liquid from (C) (light yellow color). All NMR experiments were performed in DMSO-*d*₆ solvent at ambient temperature.

experiment, a steady isolated yield (76±2%) could be reproducibly achieved (Fig. 1C). Moreover, regardless of the nature of ionic liquid studied (colored or slightly colored, before or after regeneration), no new proton signals were observed and, accordingly, only identical proton NMR spectra were obtained (Fig. 2). In addition, the result from UV–vis spectrophotometric measurements showed that, as expected, higher absorbance values were obtained for ionic liquids previously preheated by microwaves (very light

brown color) or directly recovered from the Claisen rearrangement reaction (dark brown color) (Fig. 3, curves b and c). However, no distinct new absorption bands in visible wavelengths were observed in the spectra and the nature of colored species therefore remained unresolved. Most significantly, the ionic liquid regeneration protocol developed in our laboratory appears to efficiently regenerate [b-3C-im][NTf₂] as both a newly prepared and the regenerated ionic liquids showed essentially identical UV–vis spectrum (Fig. 3, curve a). Our results on the study of thermal stability and reuse of ionic liquid clearly demonstrated that the bicyclic [b-3C-im][NTf₂] ionic liquid is a promising solvent for high-temperature organic reactions and, upon appropriate regeneration, can be recycled multiple times.

3. Conclusions

In this report, we employed a bicyclic imidazolium-based room-temperature ionic liquid, [b-3C-im][NTf₂], recently developed in our laboratory^{2a,b} as a promising solvent and successfully applied to high-temperature organic reactions such as Claisen rearrangement. Our results presented in this work unambiguously demonstrated that, in tandem with microwaves, all allyl aryl ethers rapidly converted to the desired Claisen adducts in ≤3 min and proceeded the rearrangements with high isolated yields (69–82% at 250 °C and 75–82% with Lewis acid at 200 °C). Under our experimental conditions, all rearrangement reactions were clean, no side reactions or products such as derivatives of dihydrobenzo[*b*]furan were observed, and the *ortho*- and/or *para*-Claisen adducts were the sole products. Moreover, we have also demonstrated in this report that our [b-3C-im][NTf₂] ionic liquid could be conveniently regenerated and readily reused for multiple times. In summary, this [b-3C-im][NTf₂] ionic liquid has been previously characterized and described as chemically stable room-temperature ionic liquid and, for

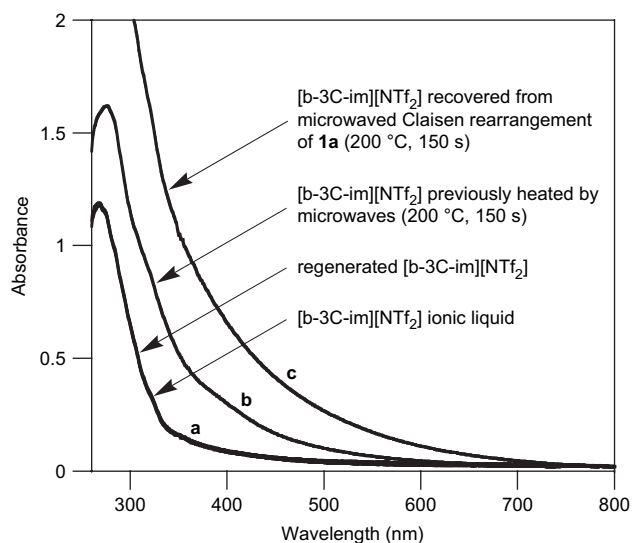


Figure 3. UV–vis spectra of: (curve a) [b-3C-im][NTf₂] ionic liquid alone (pale yellow color), (curve b) [b-3C-im][NTf₂] previously heated by microwaves at 200 °C for 150 s (very light brown color), (curve c) [b-3C-im][NTf₂] ionic liquid recovered from the Claisen rearrangement of allyl phenyl ether **1a** in the presence of MgCl₂ with heating by microwaves at 200 °C for 150 s (dark brown color), and (curve a) the regenerated [b-3C-im][NTf₂] ionic liquid (light yellow color). All spectrophotometric measurements were carried out with identical concentration (100 mM) in DMSO solvent at ambient temperature.

the work presented in this study, appears to be thermally stable for Claisen rearrangement reaction and therefore may well suit for use as promising solvent for many synthetic organic reactions.

4. Experimental

4.1. General experimental section

Flash chromatography was performed on silica gel (230–400 mesh). TLC was carried out on aluminum-backed silica plates precoated with silica (0.2 mm), which were developed using standard visualizing agents such as UV fluorescence and iodine. Unless otherwise indicated, all reactions were carried out without the aid of dry nitrogen or argon. NMR spectra were recorded on a Bruker Avance DPX 400 at 400 MHz (^1H) and 100 MHz (^{13}C) in CD_3Cl unless otherwise stated. Chemical shifts were quoted in parts per million (ppm). Melting points were determined on a Fargo MP-2D apparatus (Taiwan, ROC) and are uncorrected. UV–vis spectrophotometric measurements were carried out using a double-beam Varian's Cary 100. Solvents and reagents were obtained from commercial sources and were used without further purification.

4.2. Preparation of allyl aryl ethers (**1c**, **1e–1j**)

Among the allyl aryl ethers **1** studied in this work, allyl phenyl ether (**1a**) and allyl 2- and 4-tolyl ethers (**1b** and **1d**) were available commercially and used directly without further purification. Others (**1c**, **1e–1j**) could be readily prepared by a modified procedure of Sonnenberg.⁵ To a 25-mL round-bottomed flask containing acetonitrile (5 mL) were added substituted phenol reagent (0.5 g, 1 equiv), potassium carbonate (2 equiv), and allyl bromide (2 equiv). The reaction solution was mixed well and heated to reflux. The progress of the reaction could be monitored by thin layer chromatography (typically in 1–3 h). After the reaction, the residual potassium carbonate solid was removed by simple filtration and the solution mixture was concentrated in vacuo to afford the crude product. To this crude product was then added diethyl ether (5 mL). The ether solution was washed three times with 10% sodium hydroxide (3×1 mL) and dried over anhydrous sodium sulfate. Filtration and evaporation under reduced pressure afforded the desired product with high isolated yield (typically 82–90%). Satisfactory ^1H and ^{13}C NMR results were obtained for **1c**, **1e–1j** (for NMR spectra, see Supplementary data).

Allyl 3-tolyl ether (1c): 0.56 g (82% yield, 3 h reaction time), light yellow liquid; $R_f=0.77$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 2.32 (s, CH_3 , 3H), 4.51 (d, $J=5.3$ Hz, CH_2 , 2H), 5.25–5.42 (m, $\text{C}=\text{CH}_2$, 2H), 6.01–6.08 (m, $\text{C}=\text{CH}$, 1H), 6.70–6.77 (m, ArH, 3H), 7.17 (t, $J=7.8$ Hz, ArH, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.5, 68.7, 111.6, 115.6, 117.5, 121.7, 133.5, 139.5, 158.6; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}$ 148.0888, found 148.0892.

1-Allyloxy-2-methoxybenzene (1e): 0.55 g (83% yield, 3 h reaction time), yellow liquid; $R_f=0.60$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 3.86 (s, CH_3 ,

3H), 4.59–4.61 (m, CH_2 , 2H), 5.25–5.41 (m, $\text{C}=\text{CH}_2$, 2H), 6.04–6.11 (m, $\text{C}=\text{CH}$, 1H), 6.86–6.91 (m, ArH, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.8, 69.8, 111.8, 113.6, 117.8, 120.7, 133.4, 148.0, 149.5; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$ 164.0837, found 164.0839.

1-Allyloxy-3-methoxybenzene (1f): 0.6 g (90% yield, 3 h reaction time), yellow liquid; $R_f=0.70$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 3.77 (s, CH_3 , 3H), 4.49–4.51 (m, CH_2 , 2H), 5.25–5.41 (m, $\text{C}=\text{CH}_2$, 2H), 5.99–6.09 (m, $\text{C}=\text{CH}$, 1H), 6.47–6.52 (m, ArH, 3H), 7.16 (t, $J=8.1$ Hz, ArH, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.2, 68.8, 101.2, 106.4, 106.9, 117.6, 129.8, 133.3, 159.8, 160.1; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$ 164.0837, found 164.0840.

1-Allyloxy-4-methoxybenzene (1g): 0.57 g (86% yield, 3 h reaction time), yellow liquid; $R_f=0.79$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 3.75 (s, CH_3 , 3H), 4.46–4.48 (m, CH_2 , 2H), 5.24–5.40 (m, $\text{C}=\text{CH}_2$, 2H), 6.00–6.04 (m, $\text{C}=\text{CH}$, 1H), 6.80–6.86 (m, ArH, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.7, 69.5, 114.6, 115.7, 117.4, 133.6, 152.8, 153.9; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$ 164.0837, found 164.0835.

1-Allyloxy-2-chlorobenzene (1h): 0.59 g (89% yield, 1 h reaction time), yellow liquid; $R_f=0.77$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 4.59–4.61 (m, CH_2 , 2H), 5.28–5.47 (m, $\text{C}=\text{CH}_2$, 2H), 6.01–6.10 (m, $\text{C}=\text{CH}$, 1H), 6.86–6.92 (m, ArH, 2H), 7.16 (t, $J=7.1$ Hz, ArH, 1H), 7.35 (m, ArH, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.7, 113.8, 117.8, 121.5, 123.1, 127.6, 130.3, 132.7, 154.1; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_9\text{H}_9\text{OCl}$ 168.0342, found 168.0339.

1-Allyloxy-3-chlorobenzene (1i): 0.56 g (85% yield, 1.5 h reaction time), yellow liquid; $R_f=0.74$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 4.49–4.51 (m, CH_2 , 2H), 5.27–5.41 (m, $\text{C}=\text{CH}_2$, 2H), 5.97–6.05 (m, $\text{C}=\text{CH}$, 1H), 6.78–6.80 (m, ArH, 1H), 6.89–6.92 (m, ArH, 2H), 7.17 (t, $J=8.2$ Hz, ArH, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.0, 113.3, 115.2, 117.9, 121.0, 130.2, 132.8, 134.8, 159.3; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_9\text{H}_9\text{OCl}$ 168.0342, found 168.0343.

1-Allyloxy-4-chlorobenzene (1j): 0.55 g (83% yield, 1.5 h reaction time), yellow liquid; $R_f=0.74$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 4.48–4.50 (m, CH_2 , 2H), 5.26–5.41 (m, $\text{C}=\text{CH}_2$, 2H), 5.98–6.05 (m, $\text{C}=\text{CH}$, 1H), 6.81–6.83 (m, ArH, 2H), 7.20–7.22 (m, ArH, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 69.1, 116.0, 117.8, 125.7, 129.3, 132.9, 157.2; FAB-HRMS m/z [M] $^+$ calcd for $\text{C}_9\text{H}_9\text{OCl}$ 168.0342, found 168.0339.

4.3. Claisen rearrangement of allyl aryl ethers (**1a–j**) in [b-3C-im][NTf₂] ionic liquid by microwaves at 250 °C

To a microwave reaction vessel containing [b-3C-im][NTf₂] ionic liquid (200 μL) was added allyl aryl ether (100 mg). The vessel was placed inside a CEM Discover single-mode microwave synthesizer where it was exposed to microwaves at 250 °C (80 W) for 90–150 s. The progress of the reaction could be monitored by thin layer

chromatography. After the reaction was completed, the reaction mixture was extracted with diethyl ether three times (3×2 mL), the combined ethereal solution was dried over anhydrous sodium sulfate, filtered and then concentrated to dryness in vacuo. The desired products were purified by flash chromatography (ethyl acetate/hexane=1:6, v/v) to finally afford the corresponding rearranged allylphenols as light yellow liquids with high isolated yields (69–82%). Satisfactory ¹H and ¹³C NMR results were obtained for all desired products (for NMR spectra, see Supplementary data).

2-Allylphenol (2a): 75 mg (75% yield, 90 s reaction time), yellow liquid; $R_f=0.35$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.40 (d, $J=6.3$ Hz, CH₂, 2H), 5.00 (s, OH, 1H), 5.12–5.16 (m, C=CH₂, 2H), 5.96–6.06 (m, C=CH, 1H), 6.79–6.89 (m, ArH, 2H), 7.09–7.14 (m, ArH, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 35.0, 115.8, 116.4, 120.9, 125.3, 127.8, 130.4, 136.4, 154.0; FAB-HRMS m/z [M]⁺ calcd for C₉H₁₀O 134.0732, found 134.0730.

2-Allyl-6-methylphenol (2b): 49 mg (49% yield, 90 s reaction time), yellow liquid; $R_f=0.56$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, CH₃, 3H), 3.40 (d, $J=6.4$ Hz, CH₂, 2H), 4.97 (s, OH, 1H), 5.15–5.21 (m, C=CH₂, 2H), 5.96–6.04 (m, C=CH, 1H), 6.78 (t, $J=7.5$ Hz, ArH, 1H), 6.95 (d, $J=7.4$ Hz, ArH, 1H), 7.01 (d, $J=7.4$ Hz, ArH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.8, 35.6, 116.6, 120.4, 124.2, 124.5, 128.0, 129.4, 136.5, 152.6; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O 148.0888, found 148.0891.

4-Allyl-2-methylphenol (3b): 21 mg (21% yield, 90 s reaction time), yellow liquid; $R_f=0.43$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 2.21 (s, CH₃, 3H), 3.26 (d, $J=6.7$ Hz, CH₂, 2H), 4.58 (s, OH, 1H), 5.00–5.06 (m, C=CH₂, 2H), 5.88–5.95 (m, C=CH, 1H), 6.69 (d, $J=8.0$ Hz, ArH, 1H), 6.88 (d, $J=9.9$ Hz, ArH, 1H), 6.92 (s, ArH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.7, 39.3, 114.9, 115.3, 123.7, 127.0, 131.1, 132.2, 138.0, 152.1; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O 148.0888, found 148.0890.

2-Allyl-3-methylphenol and 2-allyl-5-methylphenol (2c): 74 mg (74% yield, a mixture of two 1.2:1 *ortho*-adducts, 120 s reaction time), yellow liquid; $R_f=0.46$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, CH₃, 3H), 2.28 (s, CH₃, 3H), 3.35–3.37 (m, CH₂, 2H), 3.41–3.43 (m, CH₂, 2H), 4.82 (s, OH, 1H), 4.88 (s, OH, 1H), 4.99–5.16 (m, C=CH₂, 4H), 5.92–6.00 (m, C=CH, 2H), 6.63–6.77 (m, ArH, 4H), 6.98–7.02 (m, ArH, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 19.5, 21.0, 30.5, 34.7, 113.3, 115.3, 116.1, 116.5, 121.6, 122.2, 122.8, 123.9, 127.0, 130.2, 135.5, 136.7, 137.9, 138.2, 153.8, 153.9; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O 148.0888, found 148.0889.

2-Allyl-4-methylphenol (2d): 77 mg (77% yield, 90 s reaction time), yellow liquid; $R_f=0.50$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 2.25 (s, CH₃, 3H), 3.36 (d, $J=6.4$ Hz, CH₂, 2H), 4.83 (s, OH, 1H), 5.12–5.17 (m, C=CH₂, 2H), 5.95–6.05 (m, C=CH, 1H), 6.70 (d, $J=8.0$ Hz, ArH, 1H), 6.90–6.92 (m, ArH, 2H); ¹³C NMR

(100 MHz, CDCl₃) δ 20.4, 35.1, 115.6, 116.3, 125.0, 128.2, 130.1, 130.9, 136.5, 151.8; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O 148.0888, found 148.0890.

2-Allyl-6-methoxyphenol (2e): 64 mg (64% yield, 90 s reaction time), yellow liquid; $R_f=0.46$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.41 (d, $J=6.8$ Hz, CH₂, 2H), 3.87 (s, CH₃, 3H), 5.02–5.09 (m, C=CH₂, 2H), 5.69 (s, OH, 1H), 5.97–6.01 (m, C=CH, 1H), 6.72–6.81 (m, ArH, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 33.8, 56.0, 108.6, 115.4, 119.4, 122.2, 125.9, 136.6, 143.4, 146.4; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O₂ 164.0837, found 164.0835.

4-Allyl-2-methoxyphenol (3e): 18 mg (18% yield, 90 s reaction time), yellow liquid; $R_f=0.43$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.31 (d, $J=6.7$ Hz, CH₂, 2H), 3.86 (s, CH₃, 3H), 5.03–5.08 (m, C=CH₂, 2H), 5.48 (s, OH, 1H), 5.91–5.97 (m, C=CH, 1H), 6.66–6.68 (m, ArH, 2H), 6.82–6.84 (m, ArH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 39.8, 55.8, 111.1, 114.2, 115.5, 121.1, 131.9, 137.8, 143.8, 146.4; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O₂ 164.0837, found 164.0835.

2-Allyl-3-methoxyphenol (2f): 55 mg (55% yield, 120 s reaction time), yellow liquid; $R_f=0.42$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.45–3.47 (m, CH₂, 2H), 3.80 (s, CH₃, 3H), 5.05–5.13 (m, C=CH₂, 2H), 5.16 (s, OH, 1H), 5.94–6.02 (m, C=CH, 1H), 6.47–6.50 (m, ArH, 2H), 7.07 (t, $J=8.2$ Hz, ArH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 27.3, 55.8, 103.3, 108.8, 113.7, 115.3, 127.5, 136.3, 155.1, 158.2; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O₂ 164.0837, found 164.0839.

2-Allyl-5-methoxyphenol (2f): 16 mg (16% yield, 120 s reaction time), yellow liquid; $R_f=0.32$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.33 (d, $J=6.3$ Hz, CH₂, 2H), 3.75 (s, CH₃, 3H), 5.09–5.16 (m, C=CH₂ and OH, 3H), 5.95–6.01 (m, C=CH, 1H), 6.40–6.46 (m, ArH, 2H), 6.98 (d, $J=8.4$ Hz, ArH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 34.5, 55.3, 102.0, 106.3, 116.2, 117.3, 130.8, 136.8, 155.0, 159.6; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O₂ 164.0837, found 164.0834.

2-Allyl-4-methoxyphenol (2g): 73 mg (73% yield, 90 s reaction time), yellow liquid; $R_f=0.29$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.36 (d, $J=6.4$ Hz, CH₂, 2H), 3.74 (s, CH₃, 3H), 4.76 (s, OH, 1H), 5.11–5.16 (m, C=CH₂, 2H), 5.95–6.02 (m, C=CH, 1H), 6.65–6.76 (m, ArH, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 35.2, 55.7, 112.6, 114.8, 115.9, 116.5, 126.5, 136.1, 148.0, 153.7; FAB-HRMS m/z [M]⁺ calcd for C₁₀H₁₂O₂ 164.0837, found 164.0835.

2-Allyl-6-chlorophenol (2h): 69 mg (69% yield, 120 s reaction time), yellow liquid; $R_f=0.65$ (ethyl acetate/hexane=1:5); ¹H NMR (400 MHz, CDCl₃) δ 3.41 (d, $J=6.5$ Hz, CH₂, 2H), 5.05–5.10 (m, C=CH₂, 2H), 5.60 (s, OH, 1H), 5.94–6.01 (m, C=CH, 1H), 6.79 (t, $J=7.8$ Hz, ArH, 1H), 7.03 (d, $J=7.5$ Hz, ArH, 1H), 7.16–7.18 (m, ArH, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 34.5, 116.1, 119.9, 120.8, 126.9, 127.8, 128.9, 136.0, 149.2; FAB-HRMS m/z [M]⁺ calcd for C₉H₉OCl 168.0342, found 168.0342.

2-Allyl-5-chlorophenol (2i'): 41 mg (41% yield, 150 s reaction time), yellow liquid; $R_f=0.48$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 3.36 (d, $J=6.3$ Hz, CH_2 , 2H), 5.11–5.17 (m, $\text{C}=\text{CH}_2$, 2H), 5.33 (s, OH, 1H), 5.94–6.01 (m, $\text{C}=\text{CH}$, 1H), 6.82–6.87 (m, ArH, 2H), 7.01 (d, $J=8.1$ Hz, ArH, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 34.5, 116.1, 116.8, 121.0, 124.0, 131.2, 132.8, 135.8, 154.6; FAB-HRMS m/z $[\text{M}]^+$ calcd for $\text{C}_9\text{H}_9\text{OCl}$ 168.0342, found 168.0345.

2-Allyl-3-chlorophenol (2i): 30 mg (30% yield, 150 s reaction time), yellow liquid; $R_f=0.39$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 3.57–3.59 (m, CH_2 , 2H), 5.07–5.12 (m, $\text{C}=\text{CH}_2$, 2H), 5.34 (s, OH, 1H), 5.91–6.01 (m, $\text{C}=\text{CH}$, 1H), 6.70–6.71 (m, ArH, 1H), 6.95–7.04 (m, ArH, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.4, 114.3, 116.1, 121.9, 124.0, 127.8, 134.6, 135.1, 155.1; FAB-HRMS m/z $[\text{M}]^+$ calcd for $\text{C}_9\text{H}_9\text{OCl}$ 168.0342, found 168.0339.

2-Allyl-4-chlorophenol (2j): 80 mg (80% yield, 120 s reaction time), yellow liquid; $R_f=0.47$ (ethyl acetate/hexane=1:5); ^1H NMR (400 MHz, CDCl_3) δ 3.35 (d, $J=6.3$ Hz, CH_2 , 2H), 5.02–5.17 (m, $\text{C}=\text{CH}_2$, OH, 3H), 5.92–6.00 (m, $\text{C}=\text{CH}$, 1H), 6.71–6.73 (m, ArH, 1H), 7.05–7.07 (m, ArH, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 34.8, 117.0, 117.1, 125.5, 127.2, 127.6, 130.1, 135.5, 152.6; FAB-HRMS m/z $[\text{M}]^+$ calcd for $\text{C}_9\text{H}_9\text{OCl}$ 168.0342, found 168.0343.

4.4. Lewis acid-promoted Claisen rearrangement of allyl aryl ethers (**1a**, **1d**, **1g**, and **1j**) in [b-3C-im][NTf₂] ionic liquid by microwaves at 200 °C

To a microwave reaction vessel containing [b-3C-im][NTf₂] ionic liquid (100 μL) were added allyl aryl ether (**1a**, **1d**, **1g**, and **1j**) (50 mg) and magnesium chloride (1 equiv). The vessel was placed inside a CEM Discover single-mode microwave synthesizer where it was stirred well and exposed to microwaves at 200 °C (60 W) for 150–180 s (for microwave reactions without the aid of Lewis acid, 9–17 min were required). The progress of the reaction was monitored by thin layer chromatography. After the reaction was completed, the reaction mixture was extracted with diethyl ether five times (5 \times 2 mL), the combined ethereal solution was dried over anhydrous sodium sulfate, filtered, and then concentrated to dryness in vacuo. The desired products were purified by flash chromatography (ethyl acetate/hexane=1:5, v/v) to afford allylphenols (**2a**, **2d**, **2g**, and **2j**) as light yellow liquids with high isolated yields (79%, 75%, 82%, and 76%, respectively). Satisfactory ^1H and ^{13}C NMR data were obtained for **2a**, **2d**, **2g**, and **2j** (see Section 4.3).

4.5. Reuse of [b-3C-im][NTf₂] ionic liquid for microwaved Claisen rearrangement of allyl 4-tolyl ether (**1d**) at 250 °C

To a microwave reaction vessel containing [b-3C-im][NTf₂] ionic liquid (400 μL) was added allyl 4-tolyl ether **1d** (100 mg, 675 μmol). The solution was mixed well and the Claisen rearrangement reaction was allowed to proceed for 90 s with temperature controlled at 250 °C by microwaves (80 W, CEM Discover). Thin layer chromatography was employed to confirm the completion of reaction. After the

reaction, the reaction mixture was extracted with diethyl ether five times (5 \times 1 mL) and the combined ethereal solution was then concentrated to dryness in vacuo. If necessary, flash chromatography (ethyl acetate/hexane=1:5, v/v) was employed to purify the desired product 2-allyl-4-methylphenol **2d** isolated as a yellow liquid. A new portion of allyl 4-tolyl ether **1d** with identical amount (100 mg) was added to the recycled ionic liquid in the reaction vessel and the same reaction cycle was repeated for a total of seven times.

Among seven cycles of ionic liquid reuse, the first three cycles gave similar and acceptable isolated yields (74%, 79%, and 77%, respectively) of the desired product **2d**. The reactions studied in fourth and fifth cycles were, however, found with incomplete conversion of reaction and therefore produced lower isolated yields (59% and 56%). Moreover, after three cycles the color of [b-3C-im][NTf₂] ionic liquid was turned brownish. This ionic liquid was therefore subjected to regeneration by employing activated charcoal in hot methanol.

To a 25-mL round-bottomed flask containing methanol (10 mL) were added the ionic liquid previously reused five times (0.4 mL) and activated charcoal (60 mg). The solution was allowed to reflux for 20 min. The resulting solution was filtered and methanol in the filtrate was removed under reduced pressure to afford [b-3C-im][NTf₂] ionic liquid. The regenerated ionic liquid returned to its original light yellow color. Using this regenerated ionic liquid as solvent to perform identical microwaved Claisen rearrangement of allyl 4-tolyl ether **1d** two more times, good isolated yields of 2-allyl-4-methylphenol **2d** were again obtained experimentally (79% and 71%, respectively).

4.6. Reuse of [b-3C-im][NTf₂] ionic liquid for Lewis acid-promoted, microwaved Claisen rearrangement of allyl 4-tolyl ether (**1d**) at 200 °C

To a reaction vessel used for microwave experiments containing [b-3C-im][NTf₂] ionic liquid (300 μL) were added allyl 4-tolyl ether **1d** (50 mg, 337 μmol) and magnesium chloride (32 mg, 337 μmol). The solution was well stirred and the Claisen rearrangement reaction was allowed to proceed for 150 s with temperature controlled at 200 °C by microwaves (80 W, CEM Discover). Thin layer chromatography was used to confirm the completion of reaction. After the reaction, the solution was mixed with dichloromethane (20 mL), filtered (to remove MgCl_2), and concentrated under reduced pressure. The resulting reaction mixture was extracted with diethyl ether five times (5 \times 1 mL) and the combined ethereal solution was then concentrated to dryness in vacuo. Flash chromatography (ethyl acetate/hexane=1:5, v/v) was employed to purify the desired product 2-allyl-4-methylphenol **2d** isolated as a yellow liquid. The ionic liquid was recycled and used directly to repeat the same rearrangement reaction; that is, a new portion of allyl 4-tolyl ether **1d** (50 mg) and MgCl_2 (32 mg) were added to the recycled ionic liquid in the reaction vessel. Both cycles of reaction gave the desired product **2d** with similar isolated yields (77% and 73%).

For the reuse experiments of [b-3C-im][NTf₂] studied in this work, the ionic liquid was regenerated after every two cycles

and a total of six reaction cycles (i.e., three regenerations) was performed. A protocol of using activated charcoal in hot methanol for the regeneration of [b-3C-im][NTf₂] ionic liquid was employed.

To a 25-mL round-bottomed flask containing methanol (7 mL) were added the colored ionic liquid (0.3 mL) and activated charcoal (40 mg). The solution was allowed to reflux for 20 min. The resulting solution was filtered and methanol in the filtrate was removed under reduced pressure to afford [b-3C-im][NTf₂] ionic liquid. This regenerated ionic liquid returned to its original light yellow color. Using this regenerated ionic liquid as the solvent to repeatedly perform identical MgCl₂-promoted, microwaved Claisen rearrangement of allyl 4-tolyl ether **1d**, good isolated yields of 2-allyl-4-methylphenol **2d** were again obtained experimentally (79%, 70%, 81%, and 75%).

4.7. Reuse of [b-3C-im][NTf₂] ionic liquid for Lewis acid-promoted, microwaved Claisen rearrangement of allyl phenyl ether (**1a**) at 200 °C

To a reaction vessel used for microwave experiments containing [b-3C-im][NTf₂] ionic liquid (300 μL) were added allyl phenyl ether **1a** (50 mg, 373 μmol) and magnesium chloride (35 mg, 368 μmol). The solution was well stirred and the Claisen rearrangement reaction was allowed to proceed for 150 s with temperature controlled at 200 °C by microwaves (80 W, CEM Discover). After the reaction, the solution was mixed with dichloromethane (20 mL), filtered, and concentrated under reduced pressure. The resulting reaction mixture was extracted with diethyl ether five times (5 × 1 mL) and the combined ethereal solution was then concentrated to dryness in vacuo. Flash chromatography (ethyl acetate/hexane=1:5, v/v) was employed to purify the desired product 2-allylphenol **2a** isolated as a yellow liquid. After every cycle of the rearrangement reaction, the ionic liquid was subjected to regeneration and used directly to repeat the same rearrangement reaction (for details in ionic liquid regeneration, see Section 4.6).

Using this regenerated ionic liquid as the solvent to repeatedly perform identical MgCl₂-promoted, microwaved Claisen rearrangement of allyl 4-tolyl ether **1d** for a total of six times, good and consistent isolated yields of 2-allylphenol **2a** were obtained experimentally (79%, 76%, 73%, 77%, 76%, and 74%, respectively).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.060.

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