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Selective O-methylation of phenols and benzyl alcohols in simple pyridinium based ionic liquids

Pranab Jyoti Das *, Jupitara Das

Department of Chemistry, Gauhati University, Guwahati 781014, India

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ABSTRACT

Synthesis of pyridinium based ionic liquids were reported and applied as catalyst for the selective O-methylation of phenols and benzyl alcohols. The reactions were carried out by using dimethylcarbonate (DMC) as the methylating agent. High selectivity, high yield and recyclability of the ionic liquids are important features of the reactions.

1. Introduction

Ionic liquids (ILs), because of their low vapour pressure, high thermal and chemical stability and good solubilising properties, are recognized as environmentally harmless media. These neoteric solvents have attracted the attention of chemists from a multitude of disciplines and the domain of their application has broadened over the years. Their unique properties coupled with their role in influencing the rate of the reaction and suppression of side products and the possibility of recovery and reuse resulted in their wide use in many reactions as catalyst as well as in dual role of a catalyst and as a solvent. Several publications report the use of IL in diverse organic synthesis [1–6].

The range of ILs continues to grow and imidazolium, ammonium, thiazolium cations are especially popular. Several procedures of their synthesis and applications have been reported [7–9]. Imidazolium based ILs are reported to be biodegradable provided that the N-alkyl group has more than four carbon atoms [10,11]. However, the use of imidazolium based ILs less attractive due to their high cost. Thus it has become necessary to look for cheaper alternatives without compromising the acceptable properties. In the course of our investigations pyridinium based ILs were found to be better alternatives because of their ease of preparation and reported biodegradability [12,13]. Several IL containing pyridinium ions have earlier been synthesized [14–17] and are reported to exhibit higher melting points, lower solubility in water and higher polarity than those containing imidazolium cations [18] and these properties have been exploited for mediating certain organic synthesis such as esterification, acetylation, cyclization, oxidative desulfurization and others [19–21].

In view of the scant use of pyridinium based ILs in organic synthesis, we explored the possibility of using simple pyridinium based ILs derived from γ-picoline for their dual role as catalyst and as solvent in the synthesis of arylmethylethers and benzylmethylethers in an environmentally benign protocol using DMC as methylating agent. Arylalkylethers are compounds of considerable interest being used as precursors in the manufacture of fragrances, dyes, pesticides, durable surface coatings, varnishes and as UV absorbers [22–24]. Classically arylalkylethers are synthesized under basic condition by Williamson's synthesis [25]. Over the years many new methods have been reported for the synthesis of arylalkylethers. Although these methods are effective most of these approaches suffer from drawbacks such as utilization of expensive metal catalysts and hindered electron rich phosphine ligands [26–29]. The need for more environmentally acceptable processes has fuelled great interest towards dialkylcarbonates as alkylating agents. This is especially true for the lightest term of the series, dimethylcarbonate (DMC), which is currently regarded as a genuine example of a green compound [30]. Further consideration of green chemistry needs the application of ionic liquid for this particular reaction. However, till date only a few literatures are available for the ionic liquid induced O-methylation of phenols by DMC. Low yield and requirement of strictly

* Corresponding author.
E-mail address: pjd23@rediffmail.com (P.J. Das).

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anhydrous and inert atmosphere are some of the shortcomings of the existing methods. So there is a scope for improvement of ionic liquid catalyzed O-methylation of phenols by DMC.

2. Results and discussion

We report here the synthesis of arylmethylethers and benzylmethylethers in good yield by the reaction of phenols and benzyl alcohols with DMC in the presence of pyridinium based ILs which was derived from γ-picoline. Three ILs namely 1-ethyl-4-methylpyridinium bromide ([1-E-4-M-Pyr]Br), 1-butyl-4-methylpyridinium bromide ([1-B-4-M-Pyr]Br) and 1-octyl-4-methyl pyridinium bromide ([1-O-4-M-Pyr]Br) were prepared by a simple one pot procedure and the yield of the products was found to be 100%. Previously the IL [1-B-4-M-Pyr]Br was synthesized by a two step metathesis procedure [18] and by refluxing in ethanol [31] but the reported yield was very low (50% only). To the best our knowledge the preparation of [1-E-4-M-Pyr]Br and [1-O-4-M-Pyr]Br was not reported earlier. The characterization data of these ILs are provided in the Supporting Information. The thermal decomposition temperature of these ILs was found to be more than 215 °C (Fig. 1) which encouraged us to use this as a catalyst to carry out high temperature O-methylation reaction using DMC. The reactions were carried out at 170 °C and the results indicated a complete selectivity for the formation of O-methylated product.

In order to optimize the reaction so as to obtain a higher yield, different ILs and other solvents like anhydrous dimethylsulfoxide and anhydrous *N*,*N*-dimethylformamide were also examined in a representative reaction of 4-nitrophenol and DMC. Table 1 shows the effect of IL and solvents on the conversion and the yield. It observed that [1-B-4-MPyr]Br is the best among the ILs used. Consequently [1-B-4-MPyr]Br was chosen as the catalyst for standardization of the procedure of O-methylation of different phenols and benzyl alcohols with DMC. Further optimization was done by varying the concentrations of IL in the model reaction of 4-nitrophenol and DMC for the formation of **2i** and screened for best results in terms of reaction time and yield of the arylmethylether. Best result was obtained with 1:1 ratio by weight of the substrate and IL at an optimum temperature of 170 °C (Fig. 2).

We then investigated the O-methylation of several types of phenols and the results indicated a dependence of reaction time on the nature of the substituents in the phenol. The presence of an electron withdrawing group on the benzene ring increases the reactivity of the substrate towards O-methylation requiring less reaction time. With 2,4-dinitrophenol and 2,4,6-trichlorophenol as substrates complete conversion (confirmed from GC-MS spectrometer) to the corresponding arylmethylether was observed in a short reaction time of about 0.5 h. However, the presence of electron releasing group on the benzene ring decreases the reactivity of the substrate towards O-methylation. In a typical procedure, appropriate phenol, DMC and [1-B-4-M-Pyr]Br were mixed and heated to 170 °C for about 0.5 to 3.5 h. The reaction was found to be highly selective towards the formation of the O-methylated product and no traces of C-methylated by product were observed. Product recovery was simple. The reaction carried out is given in Scheme 1 and the results summarized in Table 2.

Table 1
Screening for efficiency of the IL. Reaction was performed with 4-nitrophenol, DMC and appropriate ILs/solvents[a].

Entry	Ionic liquid/solvent	Temperature (°C)	Time (h)	Yield(%)[b]
1	[1-E-4-M-Pyr]Br	170	1	85
2	[1-B-4-M-Pyr]Br	170	1	87
3	[1-O-4-M-Pyr]Br	170	1	60
4	Dimethylsulfoxide	170	1	nil
5	Dimethylsulfoxide[c]	170	2	nil
6	Dimethylsulfoxide[c]	185	2	nil
7	N,N-dimethylformamide[c]	160	2	nil

[a] Reaction condition: 4-nitrophenol (1 mmol), DMC (1 mL), heat.
[b] Isolated yield.
[c] 2 mL DMC was used.

From the industrial point of view reusability of a catalyst is an important property which enhances its applicability. It has been observed that the [1-B-4-MPyr]Br as the catalyst for methylation of phenol has an added advantage as there is a possibility of recover and reuse of the IL. The catalyst was reused three times without any loss of activity and selectivity and the results are summarized in Table 3. For this study, reaction of 4-nitrophenol, DMC and [1-B-4-MPyr]Br was taken as a model reaction. The IL used in the reaction could be easily recovered as they were insoluble in diethyl ether used for extraction of the product from the reaction mixture. To recover the catalyst from reaction mixture, after the completion of the reaction, the mixture was allowed to cool and diethyl ether was added. The supernatant liquid was separated and the insoluble IL was washed with ether for three times. The combined organic phase was concentrated under vacuum and purified using column chromatography to get the pure product. The residue was dried under vacuum and desiccated for 24 h and then reused.

A comparison of results obtained in this study with some reported IL is presented in Table 4. Easy preparation of [1-B-4-M-Pyr]Br IL and simple reaction procedure are the main advantages over the others.

3. Conclusions

In summary, we have successfully synthesized three pyridinium based ILs by one pot reaction between γ-picoline and alkyl bromides. The catalysts were characterized by NMR, EIMS and TGA. It was demonstrated that [1-B-4-M-Pyr]Br is efficient as catalyst as well as solvent for O-methylation of phenols and benzyl alcohols with DMC. The process is

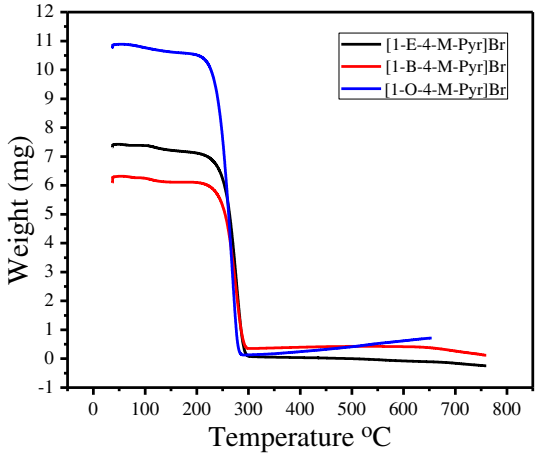


Fig. 1. Thermo Gravimetric Analysis diagram of three ionic liquids with a heating rate of 10 °C/min under nitrogen atmosphere.

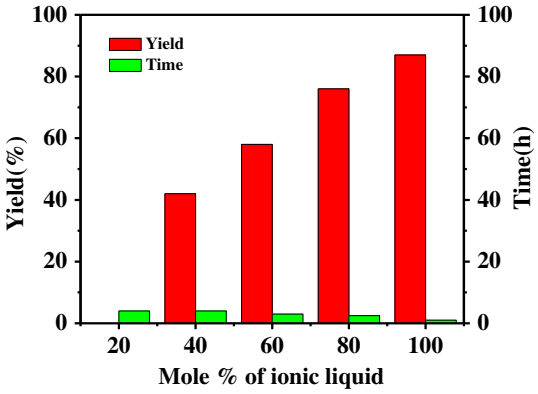
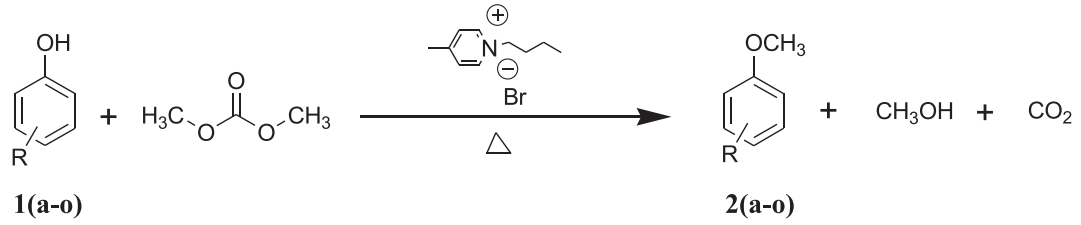


Fig. 2. Effect of amount of [1-B-4-MPyr]Br IL on the synthesis of **2i**.



Scheme 1. Synthesis of arylmethylether catalyzed by ionic liquid.

Table 2
Selective O-methylation of phenols and benzylalcohols in 1 equivalent of IL at 170 °C[a].

Entry	Substrate	Product	Time (h)	Yield[b](%)
1	2,6-Dimethylphenol(**1a**)	2,6-Dimethylanisole(**2a**)	2	70
2	4-Methoxyphenol(**1b**)	4-Methoxyanisole(**2b**)	2	75
3	2-Methoxyphenol(**1c**)	2-Methoxyanisole(**2c**)	2	75
4	3-Acetamidophenol(**1d**)	3-Acetamidoanisole(**2d**)	1	70
5	2,4,6-Trichlorophenol(**1e**)	2,4,6-Trichloroanisole(**2e**)	0.5	99
6	1-Naphthol(**1f**)	1-Methoxynaphthalene(**2f**)	2	79
7	4-Chloro-3-methylphenol(**1g**)	4-Chloro-3-methylanisole(**2g**)	2.5	78
8	2-Naphthol(**1h**)	2-Methoxynaphthalene(**2h**)	2	80
9	4-Nitrophenol(**1i**)	4-Nitroanisole(**2i**)	1	87
10	Phenol(**1j**)	Anisole(**2j**)	3.5	65
11	4-Chlorophenol(**1k**)	4-Chloroanisole(**2k**)	1	85
12	2,4-Dinitrophenol(**1l**)	2,4-Dinitroanisole(**2l**)	0.5	99
13	2-Nitrophenol(**1m**)	2-Nitroanisole(**2m**)	1	85
14	4-Chlorobenzyl alcohol(**1n**)	4-Chlorobenzylmethylether (**2n**)	2	78
15	Benzyl alcohol(**1o**)	Benzyl methyl ether(**2o**)	2	70

[a] Reaction condition: phenol (1 mmol), IL (1 mmol), DMC (1 mL), 170 °C.
[b] Isolated yield.

highly chemoselective and no C-methylated product was observed. Moreover, the catalyst is reusable with very good yield and selectivity.

4. Experimental section

4.1. General information

All products obtained were characterized by spectroscopic method such as ^{1}H NMR, ^{13}C NMR, GC–mass spectrometer and by comparing their melting points with those reported in literature. Melting points were recorded in a VMP-D model Melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in a Bruker 300 MHz Spectrometer in $CDCl_3$. In both the recordings TMS was used as the internal standard. Mass spectra were recorded in a Perkin Elmer Clarus 600 Gas Chromatograph and Clarus 600C Mass Spectrometer (Column used Elite 5MS). TGA experiments were performed using a TGA-DSC1, Mettler Toledo instrument. The samples were weighed and placed in a platinum crucible. They were then heated in a stream of nitrogen atmosphere, from room temperature to 700 °C with a heating rate usually of 10 °C/min.

4.2. General procedure for the preparation of ionic liquids

Equimolar amounts of γ-picoline and alkyl bromides (ethyl/butyl/octyl) were mixed and stirred for 24–30 h in the dark. A white coloured solid product was formed on completion of the reaction. The recovered product was found to be pure hence further purification was not necessary. The ILs obtained were found to be hygroscopic and stored in a desiccator. Yield: 100%.

4.2.1. 1-Ethyl-4-methyl pyridinium bromide

White solid; Melting Point: 97 °C; ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H ppm): 9.322 (2H, d, J = 6.6 Hz, pyr-CH), 7.756 (2H, d, J = 6.3Hz, pyr-CH), 4.803 (2H, q, J = 7.2Hz, CH_2), 2.503 (3H, s, CH_3), 1.532 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) (δ ppm): 158.53, 143.85, 128.72, 56.12, 22.03, and 17.03; MS (ES+): m/z 122.06 $[M\text{-}Br]^+$; thermal decomposition point: 503 K.

4.2.2. 1-Butyl-4-methyl pyridinium bromide

White solid; Melting Point: 99 °C; ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H ppm): 9.363 (2H, d, J = 6.6 Hz, pyr-CH), 7.840 (2H, d, J = 6.0 Hz, pyr-CH), 4.812 (2H, t, J = 7.2 Hz, CH_2), 2.577 (3H, s, CH_3), 1.972–1.872 (2H, m, CH_2), 1.381–1.282 (2H, m, CH_2), 0.853 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) (δ ppm): 158.51, 144.17, 128.70, 60.59, 33.51, 22.08, 19.09, and 13.36; HRMS (+ESI): m/z 150.1052 $[M\text{-}Br]^+$; thermal decomposition point: 498 K.

4.2.3. 1-Octyl-4-methyl pyridinium bromide

White solid; Melting Point: 55 °C; ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H ppm): 9.338 (2H, d, J = 6.3 Hz, pyr-CH), 7.893 (2H, d, J = 6.3 Hz, pyr-CH), 4.872 (2H, t, J = 7.5 Hz, CH_2), 2.645 (3H, s, CH_3), 2.022–1.941 (2H, m, CH_2), 1.300–1.204 (10H, m, CH_2), 0.824 (3H, t, J = 6.9 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.54, 144.11, 128.75, 60.93, 31.69, 31.45, 28.82, 25.84, 22.35, 22.09, and 13.87; HRMS (+ESI): m/z 206.1647 $[M\text{-}Br]^+$; thermal decomposition point: 491 K.

Table 3
Recycling of [1-B-4-MPyr]Br[a].

Cycle	1	2	3
Selectivity (%)	100	100	100
Yield (%)[a,b]	87	87	87

[a] Reaction condition: phenol (1 mmol), IL (1 mmol), DMC (1 mL), 170 °C.
[b] Isolated yield.

Table 4
Comparison of the efficiency of ionic liquid [1-B-4-M-Pyr]Br with some reported IL for the selective O-alkylation of phenols.

Entry	Catalyst	Alkylating agent	Time	Yield (%)	Ref.
1	[Bmim]Cl	DMC	1.5–6 h	99.4–99.9	[29]
2	Phosphonium based ionic liquids	Benzyl chloride	250 min	–	[32]
3	Tributylmethylammonium methylcarbonate*	DMC	–	88–94	[33]
4	[1-B-4-M-Pyr]Br	DMC	0.5–3.5 h	70–99	

* High temperature and high pressure continuous flow methylations procedure.

4.3. Selective O-methylation of phenols and benzyl alcohol

4.3.1. General procedure

A mixture of 1 mmol phenols or benzyl alcohols, 1 mL DMC and 1 mmol of IL was taken in a 10 mL RBF fitted with a reflux condenser and placed in an oil bath. The reaction mixture was heated to 170 °C under nitrogen atmosphere for reaction time indicated in Table 2. On completion of reaction, as monitored by TLC using ethyl acetate and petroleum ether (60–80 °C) as eluent, the crude product was extracted with diethyl ether (5 mL × 3), the ether extract washed with water, dried with anhydrous Na_2SO_4 and solvent removed by evaporation. The crude product obtained was purified by column chromatography on silica gel column and ethyl acetate–petroleum ether as eluent.

*4.3.1.1. 2,6-Dimethylanisole (**2a**).* Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.066–6.964 (3H, m, ArH), 3.765 (3H, s, OCH_3), 2.335 (6H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 156.86, 130.79, 128.74, 123.74, 59.56, and 16.00; GC/Ms m/z (relative intensity): 136 ($[M]^+$) (100), 121 (100), 105 (12), 91 (47), and 77 (45).

*4.3.1.2. 4-Methoxyanisole (**2b**).* Mp: 54–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 6.849 (4H, s, ArH), 3.776 (6H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 153.67, 114.58, and 55.69; GC/Ms m/z (relative intensity): 138 ($[M]^+$) (95), 123 (100), 95 (52), 92 (7), 80 (7), 77 (6), 65 (11), 64 (12), 63 (14), and 52 (10).

*4.3.1.3. 3-Acetamidoanisole (**2d**).* Mp: 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 8.531 (1H, s-broad, NH), 7.271–7.133 (2H, m, ArH), 7.021 (1H, d, J = 7.8Hz, ArH), 6.646–6.611 (1H, m, ArH), 3.726 (3H, s, OCH_3), 2.128 (3H, s, $COCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 169.26, 159.79, 139.13, 129.41, 112.24, 109.73, 105.85, 55.04, and 24.20.

*4.3.1.4. 2,4,6-Trichloroanisole (**2e**).* Mp: 60–62 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.299 (2H, s, ArH), 3.882 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 151.30, 129.96, 129.49, 128.70, and 60.78; GC/Ms m/z (relative intensity): 214 ($[M+4]^+$) (19), 212 ($[M+2]^+$) (61), 210 ($[M]^+$) (61), 199 (26), 197 (100), 195 (83), 171 (12), 165 (41), 167 (42), 111 (8), 109 (12), 107 (9), and 97 (23).

*4.3.1.5. 1-Methoxynaphthalene (**2f**).* Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 8.466–8.446 (1H, m, ArH), 7.964–7.934 (1H, m, ArH), 7.648–7.486 (4H, m, ArH), 6.906 (1H, d, J = 7.2 Hz, ArH), 4.076 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 155.30, 134.37, 127.37, 126.30, 125.79, 125.49, 125.09, 121.89, 120.11, 103.65, and 55.29; GC/Ms m/z (relative intensity): 158 ($[M]^+$) (80), 143 (43), 115 (100), 89 (12), and 63 (12).

*4.3.1.6. 4-Chloro 3-methylanisole (**2g**).* Liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.235 (1H, d, J = 8.7 Hz, ArH), 6.779 (1H, s, ArH), 6.705–6.668 (1H, m, ArH), 3.784 (3H, s, OCH_3), 2.357 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 158.02, 136.90, 129.50, 125.70, 116.35, 112.40, 55.35, and 20.28; GC/Ms m/z (relative intensity): 158 ($[M+2]^+$) (32), 156 ($[M]^+$) (100), 143 (12), 141 (37), 121 (30), 113 (31), 91 (21), 77 (51), 63 (11), and 51 (20).

*4.3.1.7. 2-Methoxynaphthalene (**2h**).* Mp: 73–75 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.805–7.749 (3H, m, ArH), 7.465 (1H, t, J = 7.2 Hz, ArH), 7.358 (1H, t, J = 7.5 Hz, ArH), 7.194–7.162 (2H, m, ArH), 3.944 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 157.58, 134.56, 129.34, 128.95, 127.61, 126.70, 126.32, 123.55, 118.66, 105.77, and 55.24; GC/Ms m/z (relative intensity): 158 ($[M]^+$) (91), 143 (11), 128 (15), 115 (100), 89 (10), and 63 (10).

*4.3.1.8. 4-Nitroanisole (**2i**).* Mp: 48 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 8.218 (2H, d, J = 9.3 Hz, ArH), 6.960 (2H, d, J = 9.3 Hz, ArH), 3.918 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 167.08, 141.70, 123.29, 116.58, and 55.89; GC/Ms m/z (relative intensity): 153 ($[M]^+$) (100), 123 (78), 107 (12), 95 (29), 92 (73), 77 (68), 64 (46), 63 (45), and 50 (23).

*4.3.1.9. Anisole (**2j**).* Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.380–7.329 (m, 2H, ArH), 7.033–6.955 (m, 3H, ArH), 3.855 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 159.45, 129.39, 120.58, 113.80, and 55.03; GC/Ms m/z (relative intensity): 108 ($[M]^+$) (100), 93 (16), 79 (17), 78 (75), 77 (20), 65 (82), 63 (13), 51 (19), 50 (12), and 39 (28).

*4.3.1.10. 4-Chloroanisole (**2k**).* Liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.291 (2H, d, J = 8.7 Hz, ArH), 6.782 (2H, d, J = 8.7 Hz, ArH), 3.792 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 158.08, 129.90, 126.70, 116.55, and 55.85; GC/Ms m/z (relative intensity): 144 ($[M+2]^+$) (32), 142 ($[M]^+$) (100), 129 (17), 127 (52), 101 (16), 99 (51), 75 (13), 73 (13), and 63 (14).

*4.3.1.11. 4-Chlorobenzyl methyl ether (**2n**).* Mp: 48–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ_H: 7.368–7.303 (4H, m, ArH), 5.127 (2H, s, CH_2), 3.800 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ: 133.68, 130.26, 129.67, 128.77, 128.45, 68.73, and 54.95; GC/Ms m/z (relative intensity): 158 ($[M+2]^+$) (9), 157 (9), 156 ($[M]^+$) (30), 155 (22), 127 (23), 125 (72), 121 (100), 91 (32), 89 (22), and 77 (21).

4.4. Reusability of ionic liquid

Before performing the reaction, we investigated the miscibility of the ILs in water and in other solvents. They were found to be miscible in water but immiscible in ether and this immiscibility made recovery of products and the IL simple. After complete extraction of the crude product with diethyl ether, the insoluble IL was dried under vacuum and stored in a desiccator for subsequent reuse. The recycled catalyst could be used for three successive runs without appreciable loss in its catalytic activity (Table 3).

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Appendix A. Supplementary data

Copies of ^{1}H, ^{13}C NMR spectra and mass spectra of ionic liquids and products.

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