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A Tandem and One-Pot Access to 2-Aroylbenzofuran and its Derivatives Using Ionic Liquid as an Efficient and Recyclable Reaction Media

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Abstract: A single step access to substituted 2-Aroylbenzofurans has been achieved under simple and eco-compatible condition via the Rap-Stoermer condensation of α -bromoketones with salicylaldehydes at room temperature in imidazolium based ionic liquids using anhydrous K_2CO_3 as a mild, inexpensive base under atmospheric conditions. Different ionic liquids were synthesized, characterized via IR, ^1H and ^{13}C NMR and were used as solvents. Among the ILs used, [Bmim] BF_4 was found to be the most effective solvent for this protocol. Shorter reaction time, excellent yields, simple work up procedure, recyclability of the ionic liquid and broad substrate scope are the major advantages of this method. The synthesized compounds were also characterized by IR, ^1H NMR, ^{13}C NMR spectroscopy.

Keywords: Ionic liquid, benzofuran, salicylaldehyde, α -bromoketones, recyclability.

Introduction

The varied nature of the chemical world requires various greener pathways in our quest towards attaining sustainability. The emerging area of green chemistry envisages minimum hazard as the performance criteria while designing new chemical processes. Rather than end-of-the-pipe remediation approach, which involves cleaning up of waste after it has been produced, the main objective is to avoid waste generation in the first place. One of the thrust areas for achieving this target is to explore alternative efficient, green and eco-friendly

reaction media to accomplish the desired chemical transformations eliminating the use of conventional organic solvents. This has led to a widespread expectation being built upon the use of ionic liquid (IL) as the solvent of choice for ‘green chemistry’ and is employed in a wide variety of reactions [1].

Ionic Liquids (ILs) are a class of organic molten electrolytes with melting point lower than $100^\circ C$. They have received significant global attention in recent years because they offer a unique environment for chemistry, biocatalysts, separation science, material synthesis, and

electrochemistry. Their negligible vapor pressure, conventional non-flammability, excellent catalytic properties, high ionic conductivity, wide electrochemical window and outstanding solvation potential form the basis for them to be classified as “green” solvents. The use of ionic liquids as reaction media and catalyst can offer a solution to the problem of solvent emission and catalyst recycling [2-3]. The results of the above findings encouraged us to explore synthesis of 2-arylbzofurans in ionic liquid.

Bzofuran and its derivatives are of interest, because of their frequent occurrence in nature and their wide range of biological and pharmaceutical applications including anti-microbial, anti-tuberculosis, anti-oxidant and anti-tumor activities [4-7]. Consequently, many research efforts have been focused on the efficient synthesis of this privileged structure such as intramolecular enolated O-arylation and thio-enolated S-arylation, intramolecular cyclization of substituted allyl-aryl ethers, [3,3]- sigmatropic rearrangement of various arenes, annulation of a furan ring onto a preexisting benzene ring [8-12]. Although many are efficient, giving good to excellent yields but some of them suffer from one or more drawbacks such as multi-step synthesis, elevated temperature, long reaction time, expensive starting materials, volatile organic solvents, external stimulant and hazardous bases [13-18]. Thus the need to develop a safe, efficient and expedient method still persists. The Rap-Stoermer reaction provides an opportunity for the efficient synthesis of bzofurans *via* base-mediated reaction of salicylaldehydes with α -bromoketones. Thus, in our endeavor to develop a novel, clean and green method for the synthesis of bzofurans herein we report ionic liquid mediated Rap-Stoermer condensation.

Experimental

All the chemicals used were of research grade (purchased from Sigma Aldrich, Merck and Acros) and were used without further purification. IR spectra were recorded on a Shimadzu FT IR- 8400S spectrophotometer. ^1H and ^{13}C NMR spectra were obtained using CDCl_3 as solvent on a JEOL JNM LA-300 spectrometer (300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR). The ^1H NMR data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm), chemical shift (multiplicity, coupling constant in Hz), and the ^{13}C NMR data in ppm (δ) from the internal standard (TMS, 0.0 ppm).

General procedure for the preparation of the imidazolium based ionic liquids

To a stirred solution of 1-methylimidazole (8.91 g, 100.0 mmol) in acetonitrile (70 mL) was added butyl bromide (110.0 mmol) dropwise at 0°C . The reaction mixture was stirred for 24-48 h at 30°C . Removal of the solvent under reduced pressure afforded crude 1-butyl-3-methylimidazolium bromide. Completion of the reaction was confirmed by ^1H NMR. The crude product was used without further purification for the next step, the anion metathesis.

General procedure for anion metathesis

To a solution of the crude 1-butyl-3-methylimidazolium bromide in acetone (70 mL) was added hexafluorophosphoric acid (10.90 g, 100.0 mmol). The reaction mixture was stirred for 24 h at room temperature. The resulting mixture was filtered. Evaporation of the solvent under reduced pressure afforded the corresponding 1-Butyl-3-methylimidazolium hexafluorophosphate. 1-Butyl-3-methylimidazolium tetrafluoroborate was also prepared using the same procedure as above except that tetrafluoro boric acid (15.08 g, 100.0 mmol) was used in place of hexafluorophosphoric acid. Progress of the

reaction was measured by TLC. Completion of the reaction was confirmed by ^1H NMR.

**1-Butyl-3-methylimidazolium
tetrafluoroborate**

Liquid. IR (KBr) cm^{-1} : 3144.76, 3071.25, 2960.55, 2935.58, 2873.65, 1571.90, 1465.51, 1382.92, 1337.38, 1170.21, 1062.29, 754.75; ^1H NMR (CDCl_3) δ : 9.51 (s, 1H, CH), 7.89 (s, 1H, CH), 7.83 (s, 1H, CH), 4.42 (t, 2H, CH_2), 4.09 (s, 3H, CH_3), 1.92 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 0.93 (t, 3H, CH_3); ^{13}C NMR (CDCl_3) δ : 137.44, 124.34, 122.98, 49.72, 36.53, 32.48, 19.62, 13.37.

**1-Butyl-3-methylimidazolium
hexafluorophosphate**

Liquid. IR (KBr) cm^{-1} : 3171.46, 3124.90, 2965.68, 2938.72, 2877.92, 1575.14, 1467.21, 1386.54, 1339.39, 1169.63, 844.79, 751.95; ^1H NMR (CDCl_3) δ : 8.95 (s, 1H, CH), 7.75 (s, 1H, CH), 7.65 (s, 1H, CH), 4.32 (t, 2H, CH_2), 4.02 (s, 3H, CH_3), 1.90 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 0.94 (t, 3H, CH_3); ^{13}C NMR (CDCl_3) δ : 137.02, 124.38, 123.00, 49.84, 36.20, 32.31, 19.58, 13.29.

**General procedure for the synthesis of
Benzofuran-2-yl(phenyl)methanone and its
derivatives**

To a mixture of compound 1a (1mmol) and 2a (1mmol) in 1 ml of ionic liquid $[\text{Bmim}]\text{BF}_4$, anhydrous potassium carbonate (2 mmol) was added and the reaction mixture was refluxed for 1h. After completion of the reaction as monitored by TLC, the product was extracted with diethyl ether (15ml $\times$ 3) leaving behind the ionic liquid that was further used in another reaction cycle. The combined organic layer was finally washed with water, dried over Na_2SO_4 and concentrated under reduced pressure to give a solid residue. All the products obtained were characterized by IR and NMR spectroscopy.

Benzofuran-2-yl(phenyl)methanone (3a)

Solid. mp: 88.5 $^\circ\text{C}$ [18] IR (KBr) cm^{-1} : 1680 (CO), 1560 (C=C); ^1H NMR (CDCl_3) δ : 8.03 (d, $J=7.2$ Hz, 2H), 7.71 (d, $J=7.6$ Hz, 1H), 7.62 (t, $J=7.6$ Hz, 2H), 7.47 ~ 7.54 (m, 4H), 7.32 (t, $J=7.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ : 184.5, 156.1, 152.2, 137.3, 133.0, 129.5, 128.6, 128.5, 127.0, 124.09, 123.4, 122.3, 116.2, 112.6.

**Benzofuran-2-yl(4-methoxyphenyl)
methanone (3b)**

Solid. mp: 95.5 $^\circ\text{C}$ [18] IR (KBr) cm^{-1} : 1677 (CO), 1556 (C=C); ^1H NMR (CDCl_3) δ : 8.11 (d, $J=7.9$ Hz, 2H), 7.71 (d, $J=8.0$ Hz, 1H), 7.61 (d, $J=8.0$ Hz, 1H), 7.51 (s, 1H), 7.47 (m, 1H), 7.29 ~ 7.33 (m, 1H), 6.99 ~ 7.02 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3) δ : 183.1, 163.7, 155.5, 152.8, 134.9, 131.9, 128.5, 127.1, 124.0, 123.4, 115.6, 113.9, 112.6, 55.6

Benzofuran-2-(p-tolyl)methanone (3c)

Solid. mp: 61 $^\circ\text{C}$ [18] IR (KBr) cm^{-1} : 1678 (CO), 1558 (C=C); ^1H NMR (CDCl_3) δ : 7.97 (d, $J=7.8$ Hz, 2H), 7.72 (d, $J=7.7$ Hz, 1H), 7.63 (d, $J=8.1$, 1H), 7.50 (s, 1H), 7.48 (t, $J=7.9$ Hz, 1H), 7.31 (t, $J=7.8$ Hz, 3H), 2.47 (s, 3H); ^{13}C NMR (CDCl_3) δ : 183.9, 154.5, 153.4, 144.3, 129.9, 129.7, 129.4, 128.7, 128.5, 122.5, 115.2, 112.5, 21.9.

**Benzofuran-2-yl(4-chlorophenyl)methanone
(3d)**

Solid. mp: 151 $^\circ\text{C}$ [13] IR (KBr) cm^{-1} : 1682 (CO), 1566 (C=C); ^1H NMR (CDCl_3) δ : 8.02 (d, $J=8.1$ Hz, 2H), 7.73 (d, $J=8.1$ Hz, 1H), 7.61 (d, $J=8.2$ Hz, 1H), 7.53 (s, 1H), 7.68 (s, 1H), 7.49 (m, 1H), 7.33 (m, 1H); ^{13}C NMR (CDCl_3) δ : 182.9, 154.7, 153.2, 136.5, 131.9, 131.0, 129.8, 129.0, 128.4, 128.1, 122.7, 115.4, 112.4.

**(5-chlorobenzofuran-2-yl)(phenyl)
methanone (3e)**

Solid. mp: 61 $^\circ\text{C}$ [18] IR (KBr) cm^{-1} : 1686

(CO), 1564 (C=C); ^1H NMR (CDCl_3) δ : 8.03 (d, $J=6.8$ Hz, 2H), 7.67 (s, 1H), 7.65 (s, 1H), 7.62 ~ 7.65 (m, 2H), 7.54 ~ 7.56 (m, 1H), 7.41 ~ 7.52 (m, 2H); ^{13}C NMR (CDCl_3) δ : 184.4, 154.8, 153.2, 136.8, 133.3, 129.6, 129.4, 128.7, 128.1, 121.8, 115.2, 113.6.

(5-chlorobenzofuran-2-yl)

(4-methoxyphenyl)methanone (3f)

Solid. mp: 61 $^\circ\text{C}$ [18] IR (KBr) cm^{-1} : 1684 (CO), 1562 (C=C); ^1H NMR (CDCl_3) δ : 8.07 (d, $J=7.9$ Hz, 2H), 7.67 (s, 1H), 7.58 (s, 1H), 7.39 ~ 7.46 (m, 2H), 6.97 ~ 7.04 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3) δ : 182.4, 163.9, 154.2, 132.0, 129.5, 128.6, 122.7, 115.5, 114.7, 113.6, 55.6.

(5-chlorobenzofuran-2-yl)(p-tolyl)

methanone (3g)

Solid. mp: 61 $^\circ\text{C}$ [18] IR (KBr) cm^{-1} : 1682 (CO), 1560 (C=C); ^1H NMR (CDCl_3) δ : 7.93 (d, $J=7.8$ Hz, 2H), 7.69 (s, 1H), 7.57 (s, 1H), 7.39 ~ 7.43 (m, 2H), 7.31 ~ 7.34 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (CDCl_3) δ : 183.5, 154.3, 153.5, 144.2, 134.2, 129.7, 129.5, 129.3, 128.5, 128.3, 122.6, 115.0, 113.6, 21.7.

(5-chlorobenzofuran-2-yl)(4-chlorophenyl) methanone (3h)

Solid. mp: 187 $^\circ\text{C}$ [20] IR (KBr) cm^{-1} : 1689 (CO), 1570 (C=C); ^1H NMR (CDCl_3) δ : 7.93 ~ 7.97 (m, 2H), 7.72 (s, 1H), 7.69 (s, 1H), 7.49 ~ 7.60 (m, 2H), 7.45 ~ 7.49 (m, 2H); ^{13}C NMR (CDCl_3) δ : 182.3, 154.8, 153.1, 150.8, 142.1, 130.8, 130.3, 129.7, 127.6, 123.8, 123.4, 122.9, 116.5, 113.7.

(6-methoxybenzofuran-2-yl)(phenyl) methanone (3i)

Solid. mp: 105 $^\circ\text{C}$ [21] IR (KBr) cm^{-1} : 1670 (CO), 1554 (C=C); ^1H NMR (CDCl_3) δ : 8.01 (d, $J=5.0$ Hz, 2H), 7.99 ~ 7.54 (m, 4H), 7.47 (s, 1H), 7.52 (s, 1H), 7.13 (d, $J=1.6$ Hz, 1H), 6.99 ~ 6.64 (m, 1H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3) δ : 184.1, 161.6, 157.8, 152.4, 137.5, 132.9, 129.7, 128.4,

123.6, 121.3, 117.7, 114.3, 95.9, 55.7.

(6-methoxybenzofuran-2-yl)

(4-methoxyphenyl)methanone (3j)

Solid. mp: 151 $^\circ\text{C}$ [21] IR (KBr) cm^{-1} : 1665 (CO), 1538 (C=C); ^1H NMR (CDCl_3) δ : 8.08 (d, $J=8.6$ Hz, 2H), 7.57 (d, $J=8.4$ Hz, 1H), 7.46 (s, 1H), 7.18 (d, $J=1.3$ Hz, 1H), 7.02 ~ 6.94 (m, 3H), 3.91 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3) δ : 182.6, 163.6, 161.3, 157.5, 152.8, 131.9, 130.5, 123.4, 120.6, 116.2, 114.7, 113.7, 95.6, 55.7, 55.5.

(6-methoxybenzofuran-2-yl)(p-tolyl)

methanone (3k)

Solid. mp: 156 $^\circ\text{C}$ [21] IR (KBr) cm^{-1} : 1667 (CO), 1532 (C=C); ^1H NMR (CDCl_3) δ : 8.01 ~ 7.89 (m, 4H), 7.72 (s, 1H), 7.34 (d, $J=7.3$ Hz, 2H), 7.17 (s, 1H), 3.87 (s, 3H), 2.42 (s, 1H); ^{13}C NMR (CDCl_3) δ : 183.7, 161.5, 157.7, 154.4, 152.5, 131.7, 130.1, 122.7, 120.3, 116.3, 115.6, 113.2, 95.6, 55.7, 21.9.

(6-methoxybenzofuran-2-yl)

(4-chlorophenyl)methanone (3l)

Solid. mp: 151 $^\circ\text{C}$ [21] IR (KBr) cm^{-1} : 1672 (CO), 1522 (C=C); ^1H NMR (CDCl_3) δ : 7.90 ~ 8.11 (m, 5H), 7.31 (d, $J=7.2$ Hz, 2H), 7.45 (ArH, s, 1H), 7.13 (d, $J=2.09$ Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (CDCl_3) δ : 183.1, 163.3, 160.9, 157.4, 155.2, 133.1, 133.1, 123.4, 120.4, 116.2, 114.3, 113.7, 95.6, 55.7.

(6-hydroxybenzofuran-2-yl)(phenyl)

methanone (3m)

Solid. mp: 161 $^\circ\text{C}$ [21] IR (KBr) cm^{-1} : 1668 (CO), 1532 (C=C); ^1H NMR (CDCl_3) δ : 8.01 ~ 7.95 (m, 2H), 7.52 (s, 1H), 7.68 ~ 7.61 (m, 2H), 7.59 ~ 7.41 (m, 4H), 7.09 (t, $J=4.4$ Hz, 2H), 5.36 (s, 1H); ^{13}C NMR (CDCl_3) δ : 182.9, 165.1, 164.5, 135.7, 134.7, 129.1, 128.7, 128.5, 128.0, 115.3, 114.9, 109.4, 101.6.

(6-hydroxybenzofuran-2-yl)

(4-methoxyphenyl)methanone (3n)

Solid. mp: 201 °C [21] IR (KBr) cm^{-1} : 1667 (CO), 1522 (C=C); ^1H NMR (CDCl_3) δ : 7.98 ~ 8.01 (m, 2H), 7.94 (s, 1H), 7.79 (d, $J=7.6$ Hz, 1H), 7.57 (d, $J=6.7$ Hz, 1H), 7.44 (s, 1H), 6.95 ~ 7.1 (m, 2H), 5.35 (s, 1H), 3.86 (s, 3H), ^{13}C NMR (CDCl_3) δ : 184.2, 165.7, 163.2, 135.9, 134.7, 129.6, 128.7, 128.5, 127.3, 115.3, 115.2, 111.1, 101.8, 55.8.

(6-hydroxybenzofuran-2-yl)(p-tolyl) methanone (3o)

Solid. mp: 213 °C [21] IR (KBr) cm^{-1} : 1660 (CO), 1518 (C=C); ^1H NMR (CDCl_3) δ : 7.83 ~ 8.17 (m, 4H), 7.69 (s, 1H), 7.23 ~ 7.47 (m, 3H), 5.37 (s, 1H), 2.44 (s, 3H), ^{13}C NMR (CDCl_3) δ : 183.2, 164.2, 135.7, 134.2, 129.1, 128.7, 128.5, 126.3, 116.2, 115.1, 109.1, 101.4, 21.7.

(6-hydroxybenzofuran-2-yl)(4-chlorophenyl) methanone (3p)

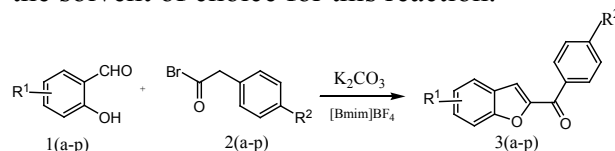
Solid. mp: 222.5 °C [21] IR (KBr) cm^{-1} : 1680 (CO), 1522 (C=C); ^1H NMR (CDCl_3) δ : 8.24 (d, $J=8.3$ Hz, 2H), 8.18 (d, $J=8.3$ Hz, 2H), 7.69 (s, 1H), 7.48 (d, $J=7.8$ Hz, 1H), 7.31 (d, $J=7.7$ Hz, 1H), 7.15 (s, 1H), 5.35 (s, 1H), ^{13}C NMR (CDCl_3) δ : 184.1, 164.6, 163.5, 136.2, 135.7, 129.4, 128.0, 128.5, 126.6, 116.2, 115.4, 112.1.

Results and discussion

In order to exploit the potential of ionic liquids as a solvent for the synthesis of 2-arylbenzofuran derivatives, we first carried out the synthesis of ionic liquids i.e. $[\text{Bmim}]\text{BF}_4$ and $[\text{Bmim}]\text{PF}_6$ via 1-methylimidazole and various alkyl halides as the starting materials [19]. The procedure for synthesis and their characterization have been discussed in detail in the experimental section. It was observed that this protocol proceeded rapidly in ionic liquids and they are superior to other reagents in terms of reaction time, temperature, yield and are enviro-economic.

Herein, the benzofuran derivatives have been synthesized by an ionic liquid mediated Rap-

Stoermer type cyclocondensation between salicylaldehydes (**1a-p**) and α -bromoketones (**2a-p**) without using any transition metal catalyst (**Scheme 1**). The study was initiated by carrying out the reaction between salicylaldehyde (**1a**) and α -bromoacetophenone (**2a**) in ethanol under reflux for overnight. No product was obtained in this. However on adding Na_2CO_3 the reaction was completed in 6h giving 65% yield of the desired Benzofuran-2-yl(phenyl) methanone (**3a**) (**Table 1, entry 1**). This shows that the condensation reaction needs an alkaline environment for the solubility and deprotonation of the substrates. The same reaction was then employed to study the effect of various solvents and bases on the product yield and time. On using solvents such as DMF, THF, toluene, acetonitrile and acetone longer reaction times were required for completion of the reaction with low yield (**Table 2, entry 2-6**). In order to avoid the use of volatile organic solvents and develop a sustainable approach, this reaction was then performed in ionic liquid $[\text{Bmim}]\text{BF}_4$. The reaction was almost quantitative in 1h as observed by TLC and Benzofuran-2-yl(phenyl) methanone (**3a**) was isolated in >90% yield through column chromatography (**Table 2, entry 8**). To investigate the use of other ionic liquids the reaction was then performed in $[\text{Bmim}]\text{PF}_6$. It was found that the reaction worked best in $[\text{Bmim}]\text{BF}_4$. In case of $[\text{Bmim}]\text{PF}_6$ the product was isolated in >80% yield and the time required for the completion of reaction was prolonged to 2h due to the hydrophobic nature of this ionic liquid [20]. Since the reaction is conducted under atmospheric conditions it is more compatible in hydrophilic ionic liquid, $[\text{Bmim}]\text{BF}_4$. Thus $[\text{Bmim}]\text{BF}_4$ was found to be the solvent of choice for this reaction.



Scheme 1

Table 1. Optimization of the solvent for the synthesis of Benzofuran-2-yl(phenyl)methanone (3a)

Entry	Solvent	Time(h)/Yield(%)
1.	Ethanol	4/65
2.	DMF	3/75
3.	Acetone	2/35
4.	Acetonitrile	2/50
5.	Toluene	3/45
6.	THF	3/66
7.	[Bmim]PF ₆	2/86
8.	[Bmim]BF ₄	1/94

The reaction was further explored using different bases. NaOH and KOH gave moderate yields (64% and 78%, respectively). The yields were found to be more than 80% when carbonates were used instead of hydroxide bases (Na₂CO₃, 86%; Cs₂CO₃, 88%; K₂CO₃, 94%). Thus K₂CO₃ was found to be the most efficient base and upon examining the influence of the amount of anhydrous K₂CO₃ on the reaction, it was found that approximately two equivalents of base were sufficient for the completion of reaction.

Table 2. Effect of various base on the synthesis of Benzofuran-2-yl(phenyl)methanone(3a)

Entry	Base	Yield(%)
1.	NaOH	42
2.	KOH	49
3.	Na ₂ CO ₃	65
4.	Cs ₂ CO ₃	88
5.	K ₂ CO ₃	94

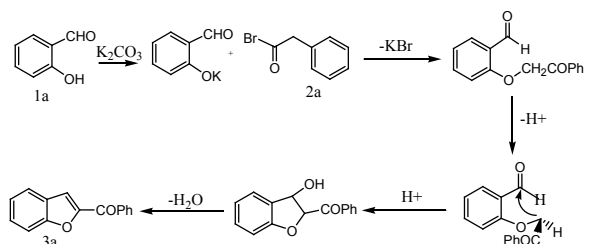
With the optimized experimental conditions, substrate generality of the reaction was investigated to study the effect of substituents on aryl rings. Many functionalities were able to

tolerate these reaction conditions and afforded the benzofuran derivatives in high yields (85–98%). Among various salicylaldehydes investigated, molecules with electron-withdrawing groups provided higher yields. Further in α -bromoketones, molecules with electron-donating group on the benzene ring gave higher yields, while those with electron-withdrawing groups led to lower yields.

Table 3. One-pot synthesis of benzofurans via various salicylaldehydes and α -bromoketones

Entry	R ¹	R ²	Product	Isolated Yield (%)	Ref
1.	H	H	3a	94	[21]
2.	H	OCH ₃	3b	96	[21]
3.	H	CH ₃	3c	92	[13]
4.	H	Cl	3d	88	[13]
5.	5-Cl	H	3e	95	[21]
6.	5-Cl	OCH ₃	3f	97	[21]
7.	5-Cl	CH ₃	3g	94	[22]
8.	5-Cl	Cl	3h	90	[22]
9.	4-OCH ₃	H	3i	88	[13]
10.	4-OCH ₃	OCH ₃	3j	90	[13]
11.	4-OCH ₃	CH ₃	3k	87	[22]
12.	4-OCH ₃	Cl	3l	86	[22]
13.	4-OH	H	3m	84	[13]
14.	4-OH	OCH ₃	3n	86	[13]
15.	4-OH	CH ₃	3o	82	[21]
16.	4-OH	Cl	3p	81	[21]

The possible mechanism of this reaction has been depicted in **Scheme 2**.

**Scheme 2**

The reaction protocol as described above is highly efficient, involves the use of an inexpensive base K_2CO_3 . Further, a very small amount of ionic liquid (1 ml/mmol) was required for the reaction and it worked as a green solvent. The cost analysis of the reaction protocol as compared to other reported methods makes it quite economical due to the recyclability of the ionic liquid. The recycling procedure involves filtration of the reaction mixture to remove the residual base and washing with diethyl ether (15 ml $\times$ 3). The product along with the impurities is isolated from the diethyl ether layer by drying over anhydrous Na_2SO_4 and evaporation under reduced pressure. The ionic liquid thus separated was dried under vacuum overnight at 80°C for reuse in the next reaction. The same process is adopted after each reaction and the recovered ionic liquid was successively used for six consecutive cycles without any significant loss in the efficiency. All the reactions were carried out under atmospheric conditions and in the hydrophilic ionic liquid $[Bmim]BF_4$ therefore, no extra precaution was needed for the exclusion of moisture.

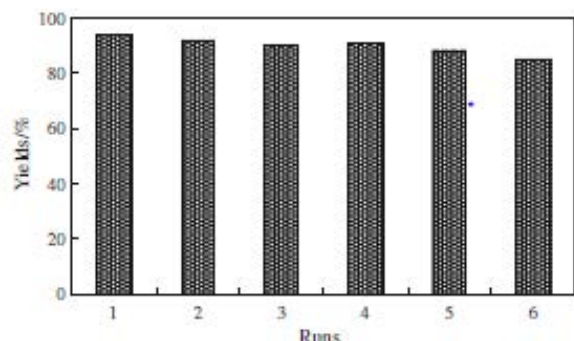


Fig.1. Recyclability of IL for the synthesis of 2-arylbenzofurans

Conclusions

In conclusion, we have developed a convenient and highly efficient ionic liquid mediated methodology for the one-pot synthesis of benzofurans at room temperature and under

mild basic conditions. The reaction is tolerant to both electron- donating as well as electron-withdrawing substituents and can be used to access various substituted benzofurans in good to excellent yields.

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