Ionic Liquid an Efficient Solvent and Catalyst for Synthesis of 1-aminoalkyl-2-naphthol and Naphthoxazine Derivatives

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ABSTRACT: *The aim of doing this research is a one-pot three-component synthesis of 1-aminoalkyl-2- naphthol and naphthoxazine derivatives using the condensation of β-naphthol with various aldehydes and amines in the presence of ionic liquid {[(secondary butyl) methyl] imidazolium bromide} {[sec-bmim]$^+$ Br$^-$, as an efficient catalyst and solvent. The catalyst was prepared according to a previously published literature procedure using 1-methyl imidazole and 2-bromo butane. Furthermore, the catalyst could be recovered conveniently and reused. This protocol has proved to be efficient in terms of good to excellent yields, lower reaction times, mild reaction conditions, eco-friendly methodology, clean reaction profiles, and a simple work-up procedure. The reactions carried out in 25˚C and mild reaction conditions without any need to high temperature.*

KEYWORDS: *Ionic liquid; {[sec-bmim]$^+$Br$^-$}; Multicomponent reaction; Aminoalkylnaphthol; Naphthoxazine.*

INTRODUCTION

Aminoalkylnaphthols are an important group of compounds because they have been found to possess useful biological activities. Hydrolysis of 1-amidoalkyl-2-naphthols leads to 1-aminomethyl-2-naphthols, compounds that exhibit hypotensive and bradycardia effects in humans [1- 3]. The synthesis of aminoalkyl naphthols is an important and useful task in organic chemistry. A straightforward method of synthesis of these compounds involves a three-component condensation of β-naphthol, an aromatic aldehyde, and amide in the presence of a catalyst.

Compounds bearing 1,3-arrangement of amino and oxygenated functional groups are frequently found in biologically important natural products [4]. Furthermore, aminoalkyl naphthols can be converted to useful synthetic building blocks [5] and 1-aminomethyl-2-naphthols, which exhibit depressor and bradycardiac activity [6]. The preparation of aminoalkyl naphthols can be carried out by multicomponent condensation of aldehydes, 2-naphthol and amine in the presence of Lewis or Brønsted acid catalysts such as chlorosulfonic acid [7]. MultiComponent Reactions (MCRs) have attracted important attention in organic synthesis as they can produce target products in a single operation without isolating the intermediates and thus reducing the energy and time of the reactions [8-12].

Ionic Liquids (IL) are a class of ionic solvents that have gained much attention in many fields of chemistry in recent years. These solvents have low melting points, negligible vapor pressures, and are stable over a wide range

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of temperatures[13] Ionic Liquids (ILs) have attracted rising interest in the last decades with a diversified range of applications. The types of ionic liquid available have also been extended to include the generations of ionic liquids with more specific and targeted properties. The ionic liquids have been found to possess a significant role as a catalyst [14-18]. They can be also used as solvents due to their unique physical and chemical properties such as non-volatility, nonflammability, thermal stability and controlled miscibility [19-21]. With this view in mind, we utilized the ionic liquid {[(secondary butyl) methyl] imidazolium bromide} {[sec-bmim]$^+$ Br$^-$} both as a catalyst and as a solvent [22] for the synthesis of the aminoalkylnaphthol derivatives via the one-pot three-component condensation of aromatic amines, aldehydes and 2-naphthol at 25˚C.

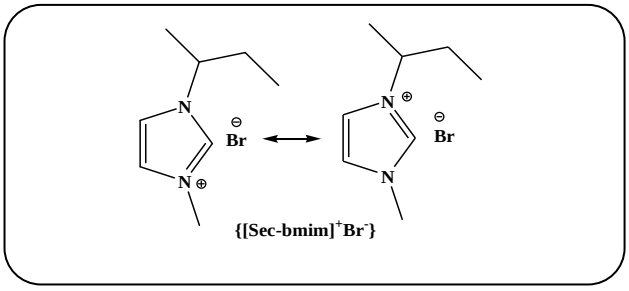
EXPERIMENTAL SECTION

^{13}C and ^{1}H NMR spectra were obtained on BrukerAvanceDpx-400 MHz instrument. All starting materials were purchased from Merck chemical company, and all were used without further purification. Melting points were determined on an electrical melting point apparatus of electrothermal IA9200with an open capillary. IR spectra were recorded on a Shimadzo-8400H, FT-IR apparatus. The rotary evaporator implement was used for evaporation of solvents. Mass-spectrometric measurements were made on an Agilent 6890 N Network GC system. The C, H, N analyses were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry, Tehran, Iran.

Synthesis of sec-butyl-3-methyl-imidazolium bromide ionic liquid {[sec-bmim]$^+$Br$^-$} 1

Ionic liquid {[sec-bmim]$^+$Br$^-$} **1** was synthesized according to previously published procedures. 1-methyl imidazole 2.46g (30mmol) was reacted with 2-bromo butane 4.52g (33mmol) under reflux condition. To this solution, 10 ml of anhydrous toluene (dried with calcium chloride as absorbent agent and refluxed for 3-4 hours) was added as a solvent. Then resulting mixture was refluxed for18 hours on a magnetic stirrer and reactions were carried out at 80°C because of the low boiling point of 2-bromo butane (b.p: 91°C). After finishing of the reaction, two phases separated using a separating funnel that ionic liquid exists in down. Then toluene was pumped out by rotary evaporation under reduced pressure. The product was got as a yellow viscous liquid and it was purified using dichloromethane and petroleum ether [22].

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.85(3H, t, *J*=7.6 Hz, CH_3), 0.88(3H, t, *J*=7.6 Hz, CH_3), 1.56 (3H, d, *J*=7.6 Hz, CH_2), 1.57 (3H, d, *J*=7.6 Hz, CH_2), 1.88 (4H, m, CH_2), 3.82 (3H, s, N-CH_3), 3.88 (3H, s, N-CH_3), 4.10 (1H, m, CH), 4.58 (1H, m, CH), 7.06 (1H, d, *J*=1.2 Hz), 7.12 (1H, d, *J*=1.2 Hz), 7.47 (1H, d, *J*=1.5 Hz, CH), 7.61 (1H, d, *J*=1.5 Hz, CH), 8.14 (1H, s, CH), 10.03 (1H, s, CH).

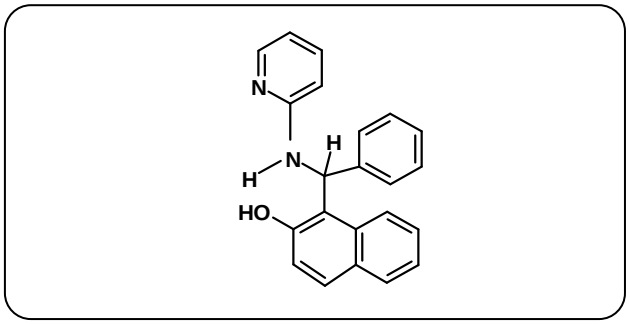


General experimental procedure for the synthesis of aminoalkyl naphthol derivatives in the ionic liquid {[sec-bmim]$^+$ Br$^-$}

Amine (1mmol), aldehyde (1mmol), and 2-naphthol (1mmol) were added to the ionic liquid (0.7 g) and stirred at room temperature (25 °C) for 3-4 hours. The progress of the reaction was monitored by TLC using *n*-hexane/ethyl acetate (1:2) and detected by UV lamp (254 & 366 nm). At the end of the reaction, the crude reaction product was diluted with 7 mL of ethyl acetate and washed with 15(3x5) mL of water because of dissolution the ionic liquid. Then two phases separated by using a separating funnel. The aqueous layer filtrate containing the ionic liquid was subjected to rotary evaporation at 100˚C under reduced pressure to provide the recovered ionic liquid to be reused several times. The organic layer was rotary evaporated; the solvent recovered by distillation and the crude product was purified by usual crystallization procedure in hot ethyl acetate/petroleum ether with the ratio (1:1). The pure products of aminoalkyl naphthol derivatives were obtained after drying under vacuum.

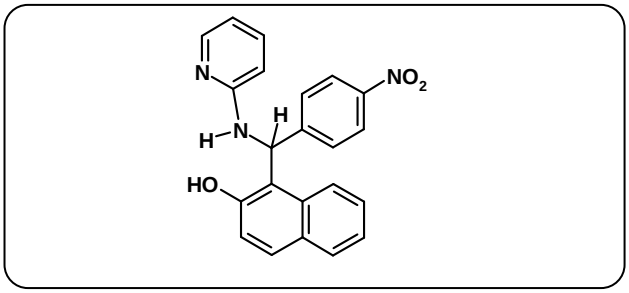
1-(phenyl (pyridine-2-ylamino)methyl)-2-naphthol 2 [23]

Colorless solid (85% yield); R_f=0.46 (n-hexane/ethyacetate =3:1); m.p. 115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.61 (1 H, d, *J*=8 Hz), 6.70 (1H, t, *J*=4 Hz) , 6.82 (1H, s), 7.26 (2H, m, *J*=8.4 Hz), 7.32 (3H, m, *J*=6.8 Hz), 7.40 (2H, d, *J*=7.6 Hz), 7.44 (1H, d, *J*=2 Hz), 7.48 (2H, m, *J*=6.4 Hz), 7.59 (1H, m, *J*=2.4 Hz), 7.63 (1H, m, *J*=6 Hz), 7.80 (1H, m, *J*=8 Hz), 8.12 (1H, d, O-H, *J*=8 Hz). ^{13}C NMR (400MHz, $CDCl_3$): δ (ppm) 53.98, 109.65, 114.31, 118.2, 120.53, 122.77, 123.09, 126.24, 126.73, 127.26, 128.39,128.74, 129.03, 129.76, 129.97, 130.09, 131.91, 133.35, 139.02, 140.98, 145.88, 154.92, 157.58. FT-IR (KBr, υ_{max}): 624, 725, 756, 825, 972, 1164, 1288 (C-N), 1388, 1535, 1620 (C=C aromatic), 1666 (C=N), 2854, 2923 (C-H aliphatic), 3055 (C-H aromatic), 3250 (N-H), 3409 (O-H) cm^{-1}.



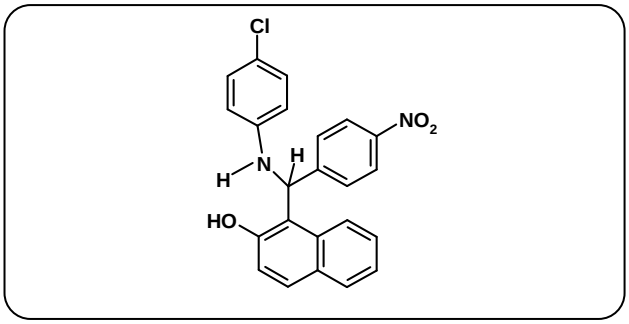
1-((4-nitro phenyl) (pyridine-2-yl amino) methyl) naphthalen-2-ol 3

Orange red solid (87% yield);R_f =0.44 (n-hexane/ethyacetate =3:1); m.p. 133ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.54 (1H, t, *J*=5.6 Hz, CH), 6.86 (1H, d, *J*=8.4 Hz), 7.26 (3H, m, *J*=8.8 Hz), 7.37 (2H, m, *J*=6.4 Hz),7.41 (1H, d, *J*=8 Hz), 7.45 (2H, d, *J*=8.8 Hz), 7.81 (2 H, t, *J*=9.2 Hz), 7.97 (1 H, d, *J*=4.4 Hz), 10.24 (1 H, s, O-H). ^{13}C NMR (400 MHz, DMSO-d_6): δ (ppm) 50.11, 109.77, 112.99, 118.96, 119.70, 123.01, 123.60, 123.91, 126.99, 127.79, 129.09, 130.10, 132.70, 137.27, 146.18, 147.76, 153.33, 153.57, 158.68. FT-IR (KBr, υ_{max}): 447, 594, 948, 1064, 1149, 1234, 1266 (C-N), 1342 (NO_2), 1434, 1512, 1557 (C=C aromatic),1600 (C=N), 2291, 2854, 2916 (C-H aliphatic), 2383, 3055 (C-H aromatic), 3348 (N-H), 3409 (O-H) cm^{-1}. MS: *m/z* 371 *(*M^+). Anal. Calcd. For $C_{22}H_{17}N_3O_3$: C, 71.15; H, 4.61; N, 11.31. Found: C, 71.09; H, 4.65; N, 11.27.



1-((4-chloro phenyl amino) (4-nitro phenyl) methyl) naphthalen-2-ol 4

Colorless crystal(65% yield);R_f =0.49 (n-hexane: ethyacetate =3:1). m.p. 154ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)3.84 (1H, s, C-NH aromatic), 7.10 (1H, m, *J*= 10.4 Hz), 7.13 (1H, m, *J*=8 Hz), 7.24 (1H, m, *J*=8 Hz), 7.35 (1H, m, *J*=16 Hz), 7.66 (1H, s), 7.69 (1H, t, *J*=2Hz), 7.76 (2H, m, *J*=10.8 Hz), 9.08 (1H, s, NH), 9.72 (1H, s, O-H). ^{13}C NMR (400 MHz, DMSO-d_6): δ (ppm) 55.36, 109.06, 119.04, 122.71, 123.08, 124.06, 126.42, 126.55, 127.98, 128.15, 128.91, 129.74, 135.03, 136.91, 155.71. MS: *m/z* 404 *(*M^+). Anal. Calcd. For $C_{23}H_{17}ClN_2O_3$: C, 68.49; H, 5.03; N, 6.66. Found: C, 68.52; H, 5.06; N, 6.68.



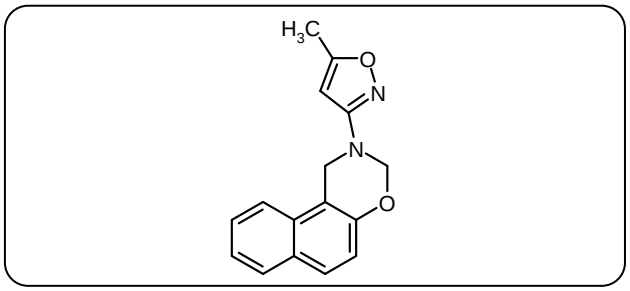
General experimental procedure for the synthesis of naphthoxazine derivatives in the ionic liquid {[sec-bmim]$^+$Br$^-$}

Amine (1 mmol) and 2-naphthol (1 mmol) was added to the ionic liquid (0.7g), aqueous formaldehyde (2 mmol) (37-41 % w/v) was added dropwise. Then the resulting mixture was stirred for 3 hours at room temperature (25°C). The completion of the reaction was monitored by TLC (n-hexane/ethyl acetate). After the finishing of the reaction, the crude reaction product was diluted with 5 mL of ethyl acetate and washed with 12(3x4) ml of water because of the dissolution of the ionic liquid. Then two phases separated by means of a separatory funnel.

The aqueous layer filtrate containing the ionic liquid was subjected to rotary evaporation at 100˚C under reduced pressure for 1 hour to provide the recovered ionic liquid to be reused several times. The organic layer was rotary evaporated; the solvent recovered by distillation and the crude product was obtained by usual crystallization procedure in hot ethyl acetate/petroleum ether with the ratio (1:1), then the pure products of naphthoxazine derivatives dried under vacuum.

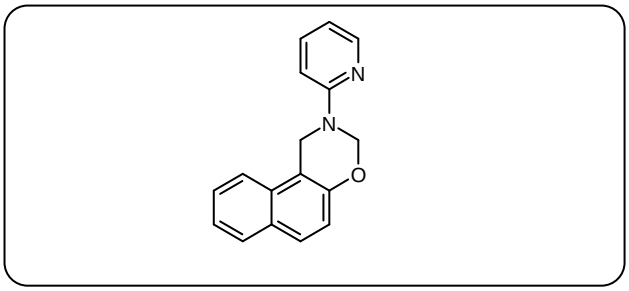
2-(5-methylisoxazole-3-yl) 2, 3-dihydro-1H-naphtho [1, 2-e][1, 3]oxazine 5

Gold crystal(81% yield); R_f =0.48 (n-hexane/ethyacetate =5:1). m.p. 90ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.50 (1H, m, *J*=1.6 Hz), 3.83 (3H, d, *J*=12.4 Hz), 4.43 (1H, m, *J*=6.8 Hz), 7.75 (1H, t, *J*=1.6 Hz), 7.89 (1H, t, *J*=1.6 Hz), 9.28 (1H, s). ^{13}C NMR (400 MHz, DMSO-d_6): δ (ppm) 10.41, 36.25, 58.12, 120.89, 121, 124.25, 136.12. FT-IR (KBr, υ_{max}): 700, 902, 956, 1050 (C-O), 1311 (C-N), 1411, 1475 (C=C aromatic), 1658 (C=N), 1998, 2090, 2329, 2592, 2908 (C-H aliphatic), 2993 (C-H arpmatic), 3440, 3795, 3919 cm^{-1}. MS: *m/z* 266 *(*M^+). Anal. Calcd. For $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.21; H, 5.27; N, 10.56.



2-(pyridine-2-yl) 2, 3-dihydro-1H-naphtho [1, 2-e][1, 3] oxazine 6

Dark red crystal (84% yield); R_f =0.59 (n-hexane:ethyacetate =4:1); m.p. 147ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.91 (2H, d, *J*=6.4 Hz), 5.43 (1H, t, *J*=4.4 Hz), 6.47 (1H, d, *J*=8.4 Hz), 6.58 (1H, t, *J*=4 Hz), 7.26 (1H, d, *J*=8.8 Hz), 7.3-7.45 (3H, m, *J*=1.6 Hz), 7.53 (1H, t, *J*=8.4 Hz), 7.75 (2H, m, *J*=4 Hz), 8.10 (1H, d, *J*=6.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 60.54, 78, 109.50, 110.43, 112.70, 121.07, 123.13, 123.27, 126.25, 127.72, 128.42, 129.10, 133.53, 138.16, 145.36, 152.56, 154.58. FT-IR (KBr, υ_{max}): 478, 740, 817, 1157 (C-O), 1242 (C-N), 1342, 1419, 1465, 1519 (C=C aromatic), 1620 (C=N), 2376, 2846, 2916 (C-H aliphatic), 3047 (C-H aromatic), 3348, 3749cm^{-1}. MS: *m/z* 262 *(*M^+). Anal. Calcd. For $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.88; H, 5.37; N, 10.62.



RESULTS AND DISCUSSION

1-methyl imidazole was reacted with 2-bromo butane under reflux condition to obtain sec-butyl-3-methyl-imidazolium bromide ionic liquid {[sec-bmim]$^+$Br$^-$}. A small excess of 2-bromo butane was used to make the full conversion of the substrate because of the low boiling point of 2-bromo butane and evaporation of it in reflux [22].

In order to optimize the reaction conditions for the above transformation, we investigated the reaction of benzaldehyde, 2-aminoaniline and β-naphthol using various amounts of the ionic liquid secondarybutyl-3-methyl-imidazolium bromide {[sec-bmim]$^+$Br$^-$} at 25ºC and the results are given below in Table 1.

On examination of Table 1, we find that 15 mg (Table 1, entry 3) of {[sec-bmim]$^+$Br$^-$} was the optimum amount to get the maximum yield of the product. When the amount of IL was gradually increased to 0.7g the isolated yield remained the same. But using more IL catalyst can lead to a dilution effect as a solvent.

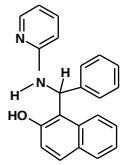
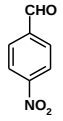
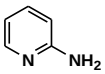
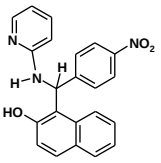
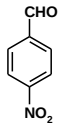
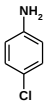
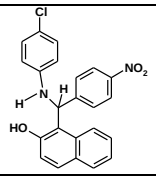
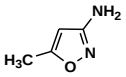
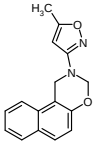
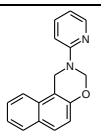
The reaction of 2-naphthol, aldehyde, and amines in IL {[sec-bmim]$^+$Br$^-$} gave aminoalkyl naphthol and naphthoxazine derivatives in good yields (Table 2). The structures of these compounds were determined by FT-IR and NMR.

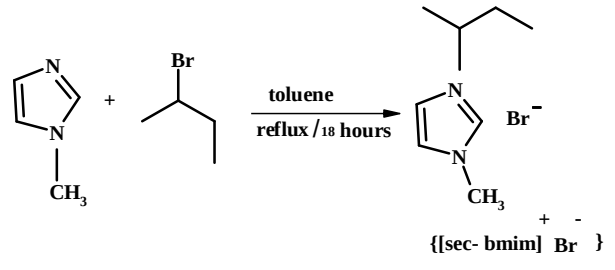
The reaction of 2-naphthol, *p*-nitrobenzaldehyde and 2-aminopyridine gave 1-((4-nitro phenyl) (pyridine-2-yl amino) methyl) naphthalen-2-ol **3**. The FT-IR spectra of this compound exhibited the absorption band of 3348 cm^{-1} (NH) and 3409 cm^{-1} (OH). The ^{1}H-NMR spectra of compound **3** showed sharp signals at δ 6.54 ppm arising from CH proton, δ 6.88-8.13 ppm from CH protons and a signal at δ 10.24 ppm from OH (Fig. 1). 20 signals

Table 1: Optimization of the IL towards the synthesis of aminoalkylnaphthol derivatives.

Entry	Amount of [secbmim]$^{+}$ Br^{-} (mg)	Yield (%) (isolated)
1	1	56
2	5	77
3	10	84
4	15	92
5	30	93
6	0.7g	93

Table 2.Synthesis of aminoalkylnaphthol and naphthoxazine derivatives with the ionic liquid {[sec-bmim]+ Br-} at 25 ºC

Entry	Aldehyde	Amine	Products	Time (h)	Yield(%)	R_f	M.p.°C
1				3	93	0.46	115°C
2				3	89	0.44	133°C
3				4	75	0.49	154°C
4				3	91	0.48	90°C
5				3	94	0.59	147°C



Scheme 1: Synthesis of ionic liquid sec-butyl-3-methyl-imidazolium bromide {[sec-bmim]$^{+}$Br^{-}}.

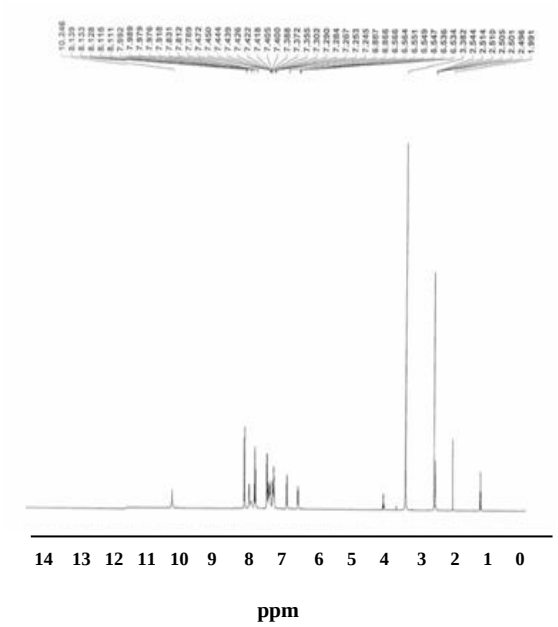


Fig. 1: ^{1}H-NMR spectra of 1-((4-nitro phenyl) (pyridine-2-yl amino) methyl) naphthalen-2-ol 3.

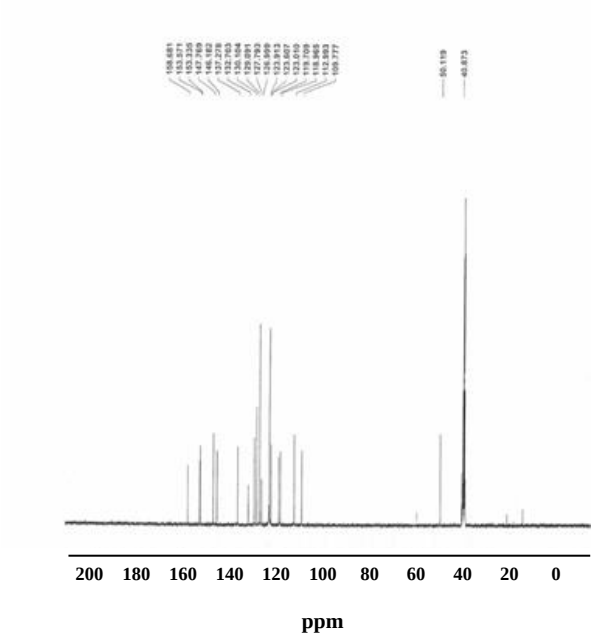


Fig. 2: ^{13}C-NMR spectra of 1-((4-nitro phenyl) (pyridine-2-yl amino) methyl) naphthalen-2-ol 3.

corresponding to all C-atoms in compound **3** were observed in the ^{13}C-NMR spectra, confirmed the structure (Fig. 2).

The ^{1}H-NMR spectra of **4** exhibited one signal at δ 3.84 for the proton of CH-N. The aromatic CH signals appeared at δ 7.10-7.76 ppm. The signals of NH and OH protons were presented at δ 9.08 and 9.72 ppm, respectively. 19 signals corresponding to all C-atoms in compound **4** were observed in the ^{13}C-NMR spectra, confirmed the structure**.** Reaction of 2-naphthol, formaldehyde and 2-aminopyridine gave 2-(pyridine-2-yl) 2, 3-dihydro-1H-naphtho [1, 2-e][1, 3] oxazine **6**. The ^{1}H-NMR spectra of compound **6** exhibited sharp signals at δ 4.91 and 5.43 ppm for protons of CH_2. 17 signals corresponding to all C-atoms in compound **6** were observed in the ^{13}C-NMR spectra, confirmed the structure**.**

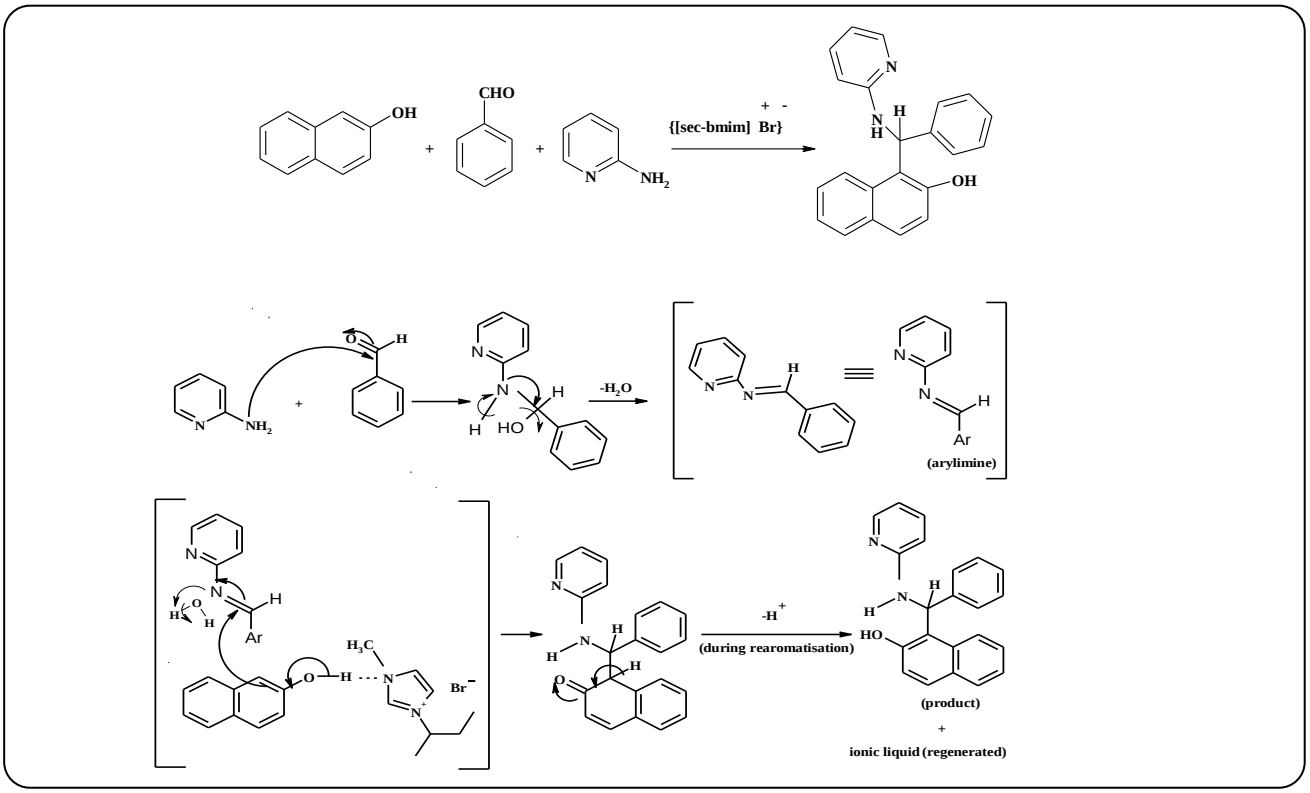
Plausible mechanisms for the production of aminoalkylnaphthol and naphthoxazine derivatives are envisaged in the Scheme (2, 3) [22].

Initially, the reaction between amine and formaldehyde forms formaldimine. The nucleophilicity of 2-naphthol increases in the presence of ionic liquid and the hydrogen bond forms between the nitrogen of the imidazolium ring of ionic liquid and hydrogen of the hydroxyl group in 2-naphthol. Then nucleophilic attack from the C_1-position of 2-naphthol towards

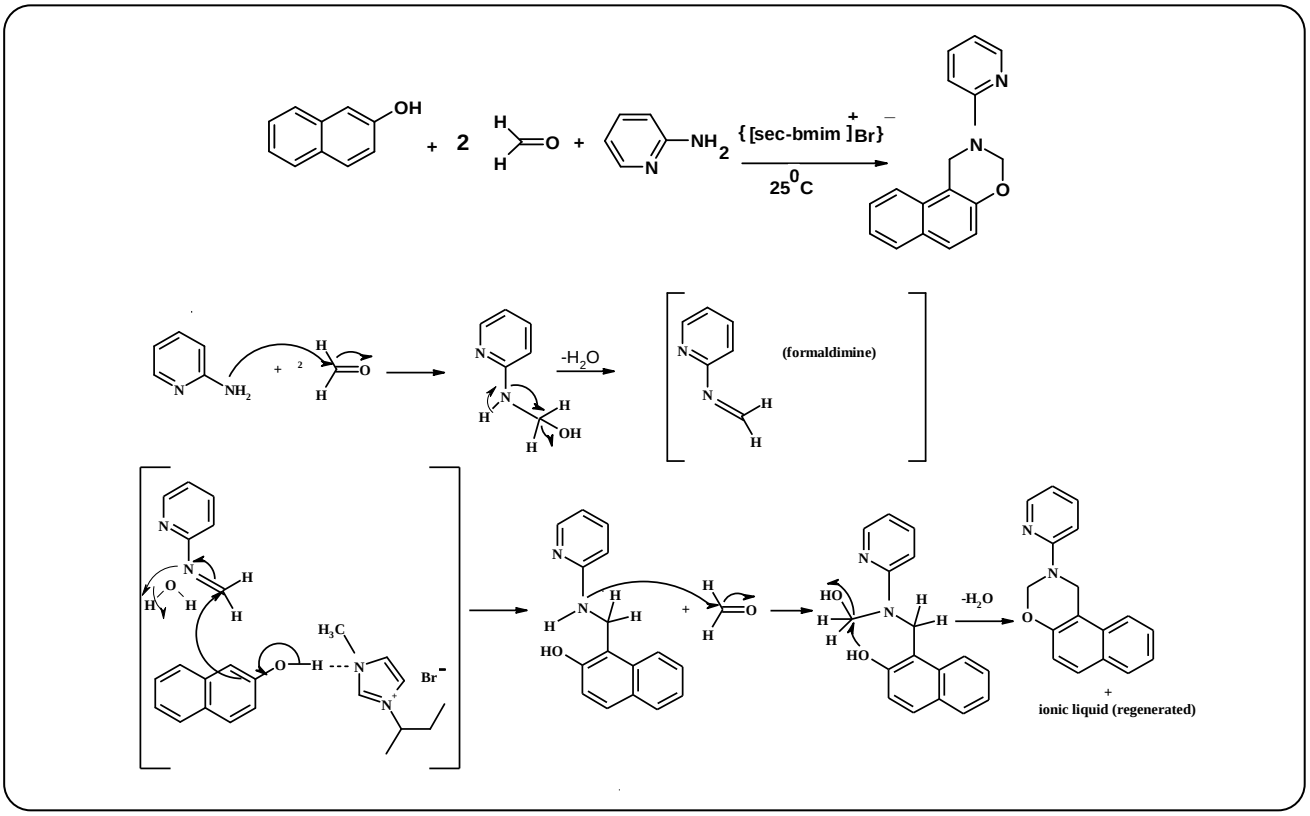
Formaldimine takes place to produce the aminoalkyl naphthol. Further attack of the amine lone pair to formaldehyde followed by the elimination of water produces the naphthoxazine. With aromatic aldehydes, the reaction stops in the aminoalkyl naphthol formation step and more attack by the nitrogen lone pair to the aldehyde carbon of carbonyl group does not occur. The more reactivity of formaldehyde is responsible for the final step of amino-alkylation followed by cyclization to naphthoxazines (Scheme 3).

CONCLUSIONS

In summary, aminoalkyl naphthol and naphthoxazine derivatives were synthesized using the ionic liquid {[sec-bmim]$^{+}$Br^{-}}. The reaction occurs simply by mixing of the reagents in the presence of ionic liquid and stirring at 25˚C. The excellent yields, mild reaction conditions, very simple purification process without the need for column chromatography and recycle ability of the catalyst, makes this methodology highly interesting. Also, the application of ionic liquid instead of organic solvents make this procedure eco-friendly because the ionic liquids have unique chemical properties such as low volatility, the ability of dissolved organic and inorganic compounds with different polarity are good alternatives to toxic and



Scheme 2: The probable mechanism of aminoalkyl naphthol derivatives formation with the ionic liquid {[sec-bmim]$^+$ Br$^-$}.



Scheme 3: The probable mechanism of naphthoxazine derivatives formation with the ionic liquid {[sec-bmim]$^+$ Br$^-$} at 25 ºC.

dangerous solvents. Also, those can be used as a catalyst in the reactions that cause to better yield of the reactions and consequently, catalyst can be easily separated from products and used for several times.

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