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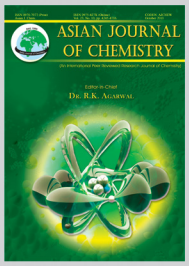

$CuCl_2$ and $FeCl_3$ as a New and Efficient Catalyst for the Oxidative Coupling of Aryl amines into 1,1′-Binaphthalene-2,2′-diamines in the Ionic Liquid Media

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A practical synthesis of 1,1′-binaphthalene-1,1′-diamines (BINAM) from α-naphthylamine is described here. The facile purification procedure of the method makes it amenable to gram scale synthesis of 1,1′-binaphthalene-1,1′-diamines with fairly high optical purity and yield of product.

Key Words: Oxidative coupling, Aryl amines, Chiral amino acid, 1,1′-Binaphthalene-2,2′-diamines, Ionic liquid.

INTRODUCTION

In the research and development of pharmaceuticals and agricultural chemicals, the demand for optically active compounds has increased more than ever[1]. There are many uses for optically pure chiral compounds[2,3] for example, chiral ligand for catalysts of various kinds of asymmetric reaction[4,5], chiral derivatizing hydrogenation of ketones[6] and transfer hydrogenation reaction[7], chiral agents for diastereometric resolution[8] or good chiral selectors for direct chiral separation[9]. 1,1′-Binaphthalene-2,2′-diamines (BINAM) and its derivatives are very popular chiral compounds that used for the above purposes and their optically pure form are needed and used word wide[10]. Several methods have been reported for synthesis of BINAM in the literature. Kocovsky employed a $CuCl_2$-mediated coupling reaction of 2-naphthylamine to BINAM in 62 % yield[11]. Ding *et al.*[12] reported an improved condition for the above coupling reaction by employing $FeCl_3{\cdot}6H_2O$ in aqueous media. By using described methods a mixture of 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) and BINAM was obtained. Buchwald *et al.*[13] offered an attractive route to synthesize chiral BINAM from optically pure BINOL *via* a palladium catalyzed amination reaction. However, this process requires several protection and deprotection steps.

In recent years, considerable attention has been focused on the application of ionic liquids to environmentally being chemical technologies because of their advantages: low vapour pressure, high thermal stability and ease of handing[14]. There are also beneficial effects of ionic liquids on rates and selectivity of important organic transformations, for example, Diels-Alder reaction[15], Wittig reaction[16], Heck reaction[17], Friedel-Crafts alkylation reaction[18], 1,3-dipolar cyclo addition reaction[19] and Suzuki cross-coupling reaction[20].

EXPERIMENTAL

General procedure: All the products were identified by comparison with authentic samples (IR, NMR, m.p.). ^{1}H NMR spectra were recorded on a Varian EM-390 NMR spectrometer operating at 90 MHz, or a Varian Unity 250 Fourier Transform NMR spectrometer operating at 250 MHz. The spectra were measured in $CDCl_3$, unless otherwise stated, relative to TMS (0.00 ppm). Mass spectra were recorded on a Shimadzu GC-MS-QP 1000PX.

Preparation of BINAM by $CuCl_2$ or $FeCl_3{\cdot}6H_2O$ in conventional organic solvents: A mixture of (4 mmol) of α-naphthylamine (**1**) and (8 mmol) of $CuCl_2$ or $FeCl_3{\cdot}6H_2O$ was finely powdered and added 20 mL of solvent and kept at boiling point temperature in reflux condition bath for 3 days. After completion of the reaction, followed by TLC, the reaction flask was cooled to room temperature. The reaction mixture was dissolved in 30 mL of methanol and quenched with 10 % HCl to pH 2. By addition of water, the precipitates of (R)-2-binaphthylamine (BINAM) (**2**) and (S)-2-binaphthylamine (BINAM) (**3**) were formed, filtered, washed with 20 mL of methanol, 20 mL of water and dried at room temperature to afford precipitates By sublimation of these precipitates at 200 °C under 1 atm the product **3** was removed, m.p. 242-244 °C. The compound **3** was characterized by IR and ^{1}H NMR analysis.

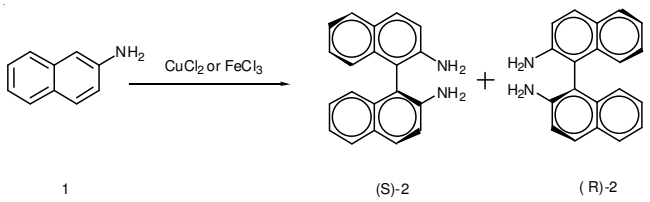
A typical procedure for preparation of compound 2 by $CuCl_2$ or $FeCl_3{\cdot}6H_2O$ in presence of optically active amino acid: In a mortar a mixture of finely powdered of L-amino acid (12 mmol) and $CuCl_2$ or $FeCl_3{\cdot}6H_2O$ (12 mmol)

was added to **1** (6 mmol) and ionic liquid (6 mmol). The mixture was ground for 20 min and kept at 100 °C for 120 min. After the completion of the reaction (monitored by TLC) 40 mL of methanol and HCl 10 % to (pH 2) was added. filtration and washing with 10 % HCl (30 mL) converted to a precipitate. The column chromatography of the precipitate on silica gel using ethylacetate:cyclohexane (10:90) as eluent gave (S)-(-)-2, colour slightly beige, m.p. 2424-244 °C $[\alpha]_D^{25}$-6.877° (C 0.453, THF).

Preparation of (1,1′-binaphthyl)-2,2′-dialkylamine: A mixture of finely powered of 2-alkylamine naphthalene (1 mmol) and $FeCl_3{\cdot}6H_2O$ (2 mmol) was ground in a mortar for 20 min and kept at 100 °C in oil bath. After completion of reaction (tested by TLC) 20 mL of chloroform was added, stirred magnetically until all mixture was dissolved, washed by 10 % HCl several times (3 × 10). The organic layer was dried gave products.

RESULTS AND DISCUSSION

Prompted by interesting features of binaphthyl amines (BINAM), we planned to set up an efficient and enantio-selective method for synthesis of these compounds. In this way, the 1:1 mixture of $CuCl_2$ and $FeCl_3{\cdot}6H_2O$ was used as an oxidant system and the reaction was conducted in ionic liquid medium in presence of a chiral amino acid (**Scheme-I**).



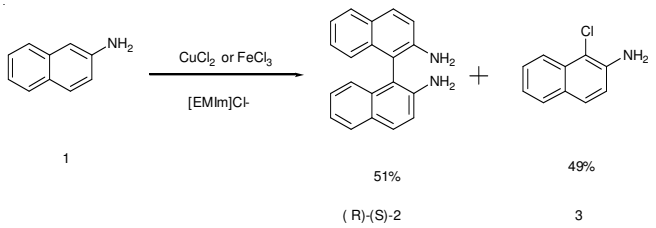
Scheme-I

Initially, in order to compare this procedure with routine methods using conventional organic solvents, we examined this oxidative coupling in the presence of different solvents and the results are summarized in Table-1. The results show that in molecular organic solvents, the reactions led to low yields but in ionic liquid media the oxidative coupling get better yields.

TABLE-1
EFFECT OF VARIOUS SOLVENTS UPON OXIDATIVE COUPLING OF **2** TO GIVE BINAM

Entry	Solvent	Temp. (ºC)	Time (day)	Yield (%)
1	Chloroform	60	3	23
2	THF	65	3	10
3	Acetone	57	3	8
4	Dichloromethane	40	3	12
5	$[BMIm]Br^-$	100	3	87
6	$[EMIm]Cl^-$	100	3	51
7	$[EMIm]\ PF_6^-$	100	3	92
8	None	150	3	–

Also, we observed that when $[EMIm]Cl^-$ is applied, as an ionic liquid, to the reaction 51 % yield of BINAM could be isolated while at the same time 49 % of 1-chloro-2-naphthyl-amine (**3**) is produced concomitantly. There is a direct relation between ratio of formation 2 against 3 with concentration of chloride ion in the ionic liquids used (**Scheme-II**).



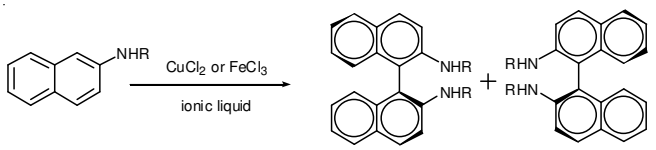
Scheme-II

In all the reactions ee % of the product was 0 %. Thus, we decided to use a chiral auxiliary amino acid in the coupling in order to increase the optical purity of product. Surprisingly, when a mixture of **1**, L-2-phenylglycine, $FeCl_3{\cdot}6H_2O$ and $[EMIm]Br^-$ was kept at 100 °C in an oven, the product S-2 was produced with high ee %. We obtain best result of non-racemic amino acid, when we examined bulk amino acid in this condition (Table-2).

TABLE-2
ENANTIO-SELECTIVE SYNTHESIS OF (S)-BINAM IN PRESENCE OF OPTICALLY ACTIVE AMINO ACID BY $FeCl_3{\cdot}6H_2O$

Entry	Amino acid	Oxidant	Temp. (ºC)	Time (min)	ee%
1	L-isoleucine	$CuCl_2$	100	120	70
2	L-pipecolinicacid	$CuCl_2$	100	120	74
3	L-*tert* leucine	$CuCl_2$	100	120	83
4	L-2-phenylglycine	$CuCl_2$	100	120	87
5	L-isoleucine	$FeCl_3{\cdot}6H_2O$	100	120	81
6	L-pipecolinicacid	$FeCl_3{\cdot}6H_2O$	100	120	86
7	L-*tert* leucine	$FeCl_3{\cdot}6H_2O$	100	120	87
8	L-2-phenylglycine	$FeCl_3{\cdot}6H_2O$	100	120	93

We have then used various N-alkyl-naphthylamines as starting compounds for the oxidative couplings under this condition (**Scheme-III** and Table-3).



Scheme-III

TABLE-3
ENANTIO-SELECTIVE SYNTHESIS OF (S)-(-)-2-ALKYLAMINONAPHTHALENE IN PRESENCE OF OPTICALLY ACTIVE AMINO ACIDS BY $FeCl_3{\cdot}6H_2O$ IN THE IONIC LIQUID

Entry	Amino acid	R	Temp. (ºC)	Time (h)	Yield (%)	ee%
1	L-*tert* leucine	Ethyl	100	1	90	89
2	L-2-phenyl glycine	Ethyl	100	1	92	87
3	L-*tert* leucine	Isobutyl	100	3	86	85
4	L-2-phenyl glycine	Isobutyl	100	3	87	87
5	L-*tert* leucine	Hexyl	100	3	75	93
6	L-2-phenyl glycine	Hexyl	100	3	70	95
7	L-*tert* leucine	Cyclohexyl	100	8	70	70
8	L-2-phenyl glycine	Cyclohexyl	100	8	68	71

In conclusion, in this study we have discovered a new method for oxidative coupling of 2-naphthylamines with the highest chemical yield and ee %.

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