5. Summary and Conclusions

To conclude, we have prepared ionic liquid [EtPy][HSO₄] and used it as an efficient and recyclable catalyst for developing a simple and efficient procedures for the synthesis of N-heterocyclic compounds. The class of compounds include indoles, bis(indolyl)methanes and imidazoles. Indoles were prepared by a two steps synthesis. First step was hydrazone formation and second step was cyclization of hydrazones to indoles on reaction with [EtPy][HSO₄] (4). Ionic liquid N-ethylpyridinium hydrogen sulfate (4) was effectively applied for the synthesis of hydrazones by the reaction of phenylhydrazine (5) /dinitrophenylhydrazine (6) with ketones (aryl/alkyl) (Scheme 5.1). Seven hydrazones namely N-Cyclohexylidene-N’-phenylhydrazine (8), 2-[1-(phenylhydrazono)ethyl]phenol (13), 2-[1-(2,4-Dinitrophenylhydrazono)ethyl]phenol (14), N-(sec-Butylidene)-N’-(2,4-dinitrophenyl)hydrazine (15), N-(2-Bromo-1-methylethylidene)-N’-(2,4-dinitrophenyl)hydrazine (16), N-(sec-Butylidene)-N’-phenylhydrazine (17), N-(2,4-Dinitrophenyl)-N’-(1-phenylethylidene)hydrazine (18) were prepared.

![Scheme 5.1: Ionic liquid catalyzed synthesis of 2-substituted indoles](image-url)
In the second step hydrazones were cyclized to their corresponding indoles on reaction with ionic liquid (4) by stirring at 120 °C for 30 minutes (Scheme 5.1). Eight derivatives synthesized included; 2,3,4,9-tetrahydro-1H-carbazole (20), 2-(1H-indol-2-yl)-phenol (21), 2-ethyl-1H-indole (22), 2- (5,7-dinitro-1H-indol-2-yl)-phenol (23), 2-ethyl-5,7-dinitro-1H-indole (24), 2-bromomethyl-5,7-dinitro-1H-indole (25), 5,7-dinitro-2-phenyl-1H-indole (26), 5,7-dinitro-1H-indole-2-carbaldehyde (28) have also been prepared from 2-bromomethyl-5,7-dinitro-1H-indole (25) using QCC (27) as an oxidizing agent to further increase the scope of the developed methodology.

Bis(indolyl)methanes were also synthesized from indoles and aldehydes (aromatic/aliphatic) using ionic liquid N-ethylpyridinium hydrogen sulfate (4) as a catalyst in aqueous media (Scheme 5.2). Seven derivatives namely; 3,3′-bis(indolyl)phenylmethane (31), 3,3′-bis(indolyl)-4-hydroxyphenylmethane (36), 3,3′-bis(indolyl)-4-chlorophenylmethane (37), 3,3′bis(indolyl)-2-furanylmethane (38), 3,3′-bis(indolyl)-2-nitrophenylmethane (39), 3,3′-bis(5,7-dinitro-2-phenyl-1-H-indolyl)-4-hydroxyphenylmethane (40), 3,3′-bis(5,7-dinitro-2-phenyl-1-H-indolyl)-4-chlorophenylmethane (41) been synthesized and screened for their antibacterial potentials. Amongst these all 3,3′-bis(indolyl)-4-hydroxyphenylmethane (36) was found to be most active against *E coli* and *Bacillus subtilis*.

Scheme 5.2: Bis(indolyl)methane synthesis in presence of ionic liquid N-ethylpyridinium hydrogen sulfate (4)
Synthesized ionic liquid N-ethylpyridinium hydrogen sulfate (4) was finally used as catalyst for synthesis of imidazole derivatives by the reaction of benzil (42), ammonium acetate (43) and aldehydes (Scheme 5.3). The derivatives synthesized were four in number and included; 2-(2-nitrophenyl)-4,5-diphenyl-1H-imidazole (44), 2,4,5-triphenyl-1H-imidazole (50), 2-(4-chloro-phenyl)-4,5-diphenyl-1H-imidazole (51), 4-(4,5-diphenyl-1H-imidazol-2-yl)phenol (52).

**Scheme 5.3: Ionic liquid (4) catalyzed synthesis of imidazole derivatives in ethanol**

Pyrrole derivatives have been synthesized by the C-N coupling reaction in presence of carbon catalyst (53). C-N coupling reaction of 2,4-dicarbonyl compound, benzoin (42) and ammonium acetate (43) in presence of carbon catalyst C_{DPR} (53) have been carried out in ethanol to obtain the 2,3,4,5-tetrasubstituted pyrrole derivatives (Scheme 5.4). Seven derivatives were synthesized by this methodology which included; 2-Methyl-4,5-diphenyl-1H-pyrrole-3-carboxylic acid methyl ester (56), 2-methyl-4,5-diphenyl-1H-pyrrole-3-carboxylic acid ethyl ester (63), 1-(2,4,5-triphenyl-1H-pyrrol-3-yl)-ethanone (64), phenyl-(2,4,5-triphenyl-1H-pyrrol-3-yl)methanone (65), 1-(2-methyl-4,5-diphenyl-1H-pyrrol-3-yl)-ethanone (66), 1-(2-ethyl-4,5-diphenyl-1H-pyrrol-3-yl)-propan-1-one (67) and 2-ethoxy-4,5-diphenyl-1H-pyrrol-3-carboxylic acid ethyl ester (68).
Scheme 5.4: $\text{CDPR} \ (53)$ catalyzed C-N coupling reaction of benzoin (42), 2,4-dicarbonyl compound and ammonium acetate (43) leading to pyrrole formation

$\text{CDPR} \ (53)$ has also been used as catalyst for C-N coupling reaction of 2,5-dicarbonyl compounds with primary (aliphatic/aromatic) amines leading to formation of tri-substituted pyrrole derivatives (Scheme 5.5). Six derivatives synthesized by this methodology include; 1-benzyl-2,5-dimethyl-1H-pyrrole (71), 2,5-dimethyl-1-propyl-1H-pyrrole (77), 1-butyl-2,5-dimethyl-1H-pyrrole (78), 2,5-dimethyl-1-p-tolyl-1H-pyrrole (79), 2,5-dimethyl-1-(4-nitro-phenyl)-1H-pyrrole (80) and 1-(4-chloro-phenyl)-2,5-dimethyl-1H-pyrrole (81).

Scheme 5.5: $\text{CDPR} \ (53)$ catalyzed C-N coupling reaction of hexan-2,5-dione (69) with primary amines (aliphatic/aromatic) leading to pyrrole formation

The use of ionic liquid was beneficial in terms of recycling and avoiding the use of volatile organic solvents. Also their miscible nature promotes their use in aqueous solution. The organic counterpart may provide beneficial in these reactions to promote the solubility of organic compounds in water. This property also promotes their easy separation from the products. Also, carbon catalyst (heterogeneous in nature) is easy to separate from the reaction mixture. This property can be further exploited to promote the recycling of such catalytic systems.