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Qinoxaline III. Synthesis Of Quinoxaline Derivatives Over Highly Efficient And Reusable Bronsted Acidic Ionic Liquids

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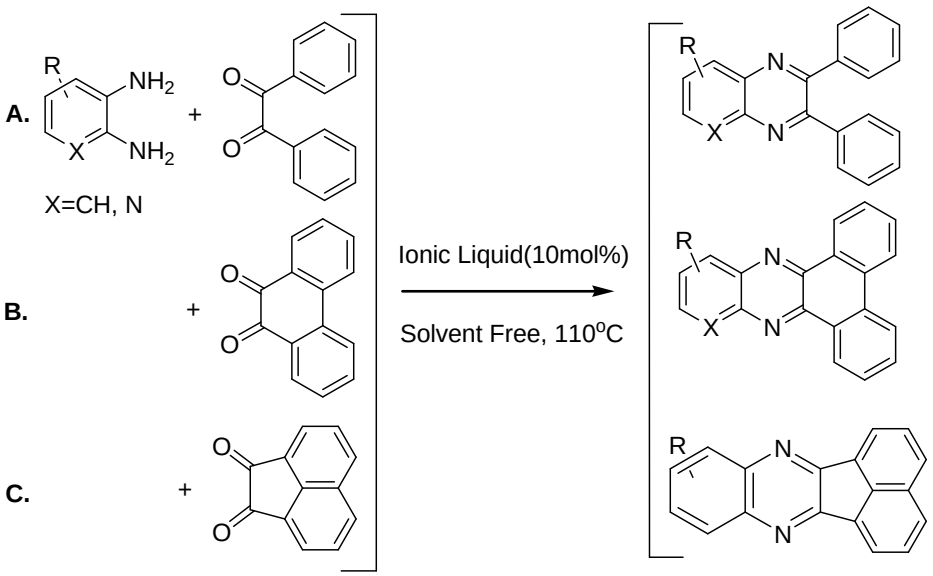
Abstract : A simple, highly efficient and green procedure for the preparation of quinoxaline in the presence of catalytic amount of ionic liquid of imidazolium salts is described. Using this method, quinoxaline derivatives as biologically interesting compounds are produced in high to excellent yields and short reaction times. Environmentally benign, simple methodologies, easy workup procedure, clean reaction, short reaction time, high yield and easy preparation of the catalysts are some advantages of this work.
Keywords: Quinoxalines synthesis, Bronsted acidic ionic liquids (BAILs), green chemistry.

1. Introduction

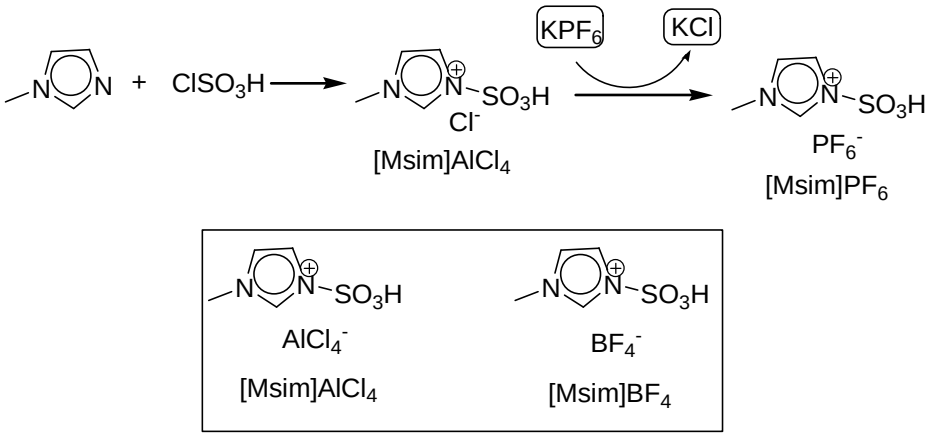
Quinoxaline derivatives are a very important class of nitrogen-containing compounds and have been widely used in dyes[1],pharmaceuticals[2] and electrical/photochemical materials[3]. Quinoxaline ring moiety constitute part of the chemical structures of various antibiotics such as Echinomycin, Levomycin and Actinoleutin[4] that are known to inhibit growth of gram positive bacteria and are active against various transplantable tumors. A number of synthetic strategies have been developed for the preparation of substituted quinoxalines[5-8]. By far, the most common method relies on the condensation of an aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid for 2–12h giving 34–85% yields[9]. More *et al* reported greener method for the synthesis of quinoxaline derivatives in green solvents ($EtOH/H_2O$), using cerium (IV) ammonium nitrate as catalysts[10]. 2,3-Disubstituted quinoxalines have also been prepared by Suzuki–Miyaura coupling reaction[11], condensation of o-phenylenediamines and 1,2-dicarbonyl compounds in MeOH/AcOH under microwave irradiation[12], iodine catalyzed cyclocondensation of 1,2- dicarbonyl compounds and substituted *o*-phenylene diamines in DMSO[13], CH_3CN[14]. Different catalysts used for quinoxaline synthesis such as Microwave/I_2[15], I_2[16], Ultrasound Irradiaton[14], Citric acid[17], ionic liquid[18] and phenol[19].

Nevertheless, many of the reported methods are associated with one or more of the following drawbacks: low yields, long reaction times, the use of large amount of catalyst, the use of toxic or expensive catalysts, and inefficiency of method.



Scheme 1. Quinoxalines synthesis by the ionic liquid of imidazolium salts.

Ionic liquids have received considerable interest as eco-friendly solvents, catalysts and reagents in organic synthesis because of their unique properties, such as low volatility, non-flammability, high thermal stability, negligible vapor pressure and ability to dissolve a wide range of material. Brønsted acidic ionic liquids (BAILs), with the useful characteristics of solid acids and mineral liquid acids, have designed to replace the traditional mineral liquid acids like sulfuric acid and hydrochloric acid in chemical procedures. We synthesized two ionic liquid of imidazolium salts, 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) {[Msim]PF_6} and 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate {[Msim]BF_4} as new ionic liquids (**Scheme 2**). We wish to use them as effective catalysts for different organic transformations. Herein, we have found that the preparation of quinoxalines derivatives can be efficiently performed in the presence of these ionic liquids under eco-friendly reaction conditions.



Scheme 2. The preparation of the ionic liquid of imidazolium salts

Design of highly efficient chemical reactions, which provide maximum structural complexity and diversity with a minimum number of synthetic steps to assemble compounds, is a major challenge of modern drug discovery. Recently, multicomponent reactions have emerged as a highly valuable synthetic tool in the context of modern drug discovery. Atom economy and convergent character, simplicity of a one-pot procedure, possible structural variations, accessible complexity of molecules, and very large number of accessible compounds are among the described advantages of multicomponent reactions[21]. Thus, they are perfectly amenable to automation for combinatorial synthesis[22].

Having the above points in mind, we report here our results on the efficient solvent-free synthesis of 2,3-diarylquinoxalines, dibenzo[a,c]phenazines and acenaphto[20] quinoxalines in the presence of a catalytic amount of ionic liquids 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl}, 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) {[Msim]PF_6} or 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate {[Msim]BF_4} under solvent-free conditions (Scheme 2). Interestingly, these methods for the preparation of the quinoxalines derivatives have none of the above-mentioned drawbacks at all.

2.Results and discussion

At first, ionic liquid 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} was prepared by the reaction of imidazole (1 eq.) with chlorosulfonic acid (2 eq.) in CH_2Cl_2 (Fig. 1) [5]. In the next step, 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} was prepared by the reaction of 1-methylimidazole with chlorosulfonic acid in CH_2Cl_2 with almost 100% atom economy[6-10]. Then, the other ionic liquid of imidazolium salts, 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) {[Msim]PF_6} and 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate {[Msim]BF_4},were prepared by anion exchange procedure (**Scheme 2**). As it is shown in **Scheme 2**, [Msim]Cl was reacted with Lewis acids KPF_6 and $NaBF_4$ to afford ionic liquids [Msim]PF_6 and [Msim]BF_4, respectively. The structures of the catalysts were identified by ^1H, ^{13}C and ^{31}P NMR as well as mass spectra. The corresponding spectral data are reported in the Experimental section.

In another study, to confirm that [Msim]Cl was completely converted to [Msim]BF_4, a solution of $AgNO_3$ in distilled water was added to a solution of [Msim]BF_4 in distilled water. The absence of AgCl precipitate indicates complete conversion of the [Msim]Cl to [Msim]BF_4.

In our initial study on the applicability of the BAIL in organic synthesis, we investigated the preparation of 2,3-diarylquinoxalines from benzene-1,2-diamines and 1,2-dicarbonyl compounds in the presence of them (**Scheme 1**). For this purpose, the condensation of 2,3-diphenylquinoxaline (1 mmol) with benzil (1 mmol) was examined using different amounts of [Dsim]Cl, [Msim]PF_6 or [Msim]BF_4 at various temperatures under solvent-free conditions. The results are summarized in Table 1. Interestingly, these catalysts were highly efficient, and 10 mol% of them was sufficient to afford the product in excellent yields and in very short reaction times at 110 °C (Table 1, entry 3). No improvement in the reaction results was observed by increasing the amount of the catalysts and the temperature. The solvent-free condensation was also tested at 110 °C without catalyst in which the reaction did not significantly progress even after long reaction time (12 h).

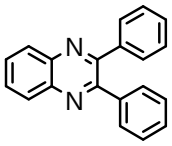
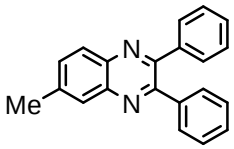
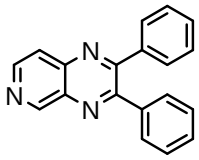
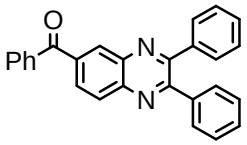
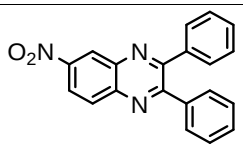
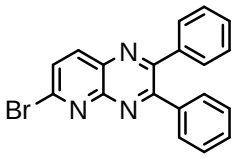
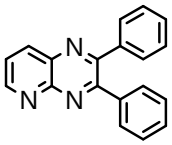
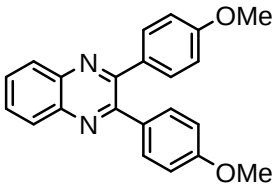
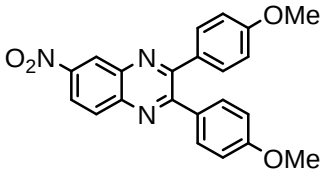
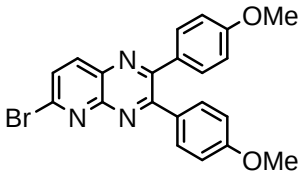
Table 1. Effect of amounts of the catalysts and temperature on the condensation of phenylenediamine (1 mmol) with benzil) (1 mmol).

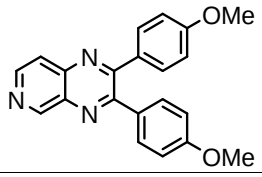
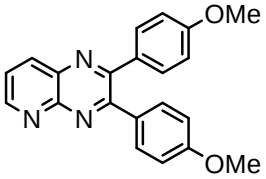
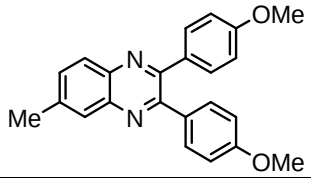
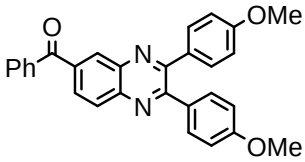
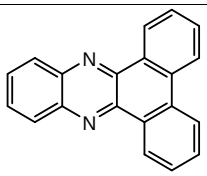
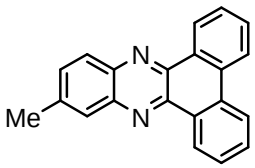
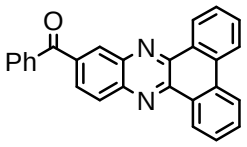
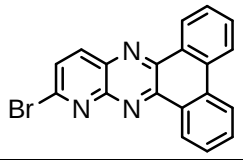
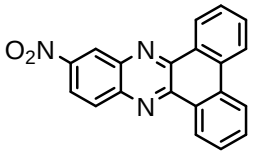
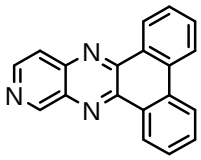
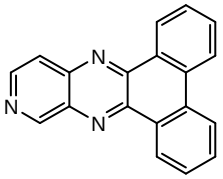
Entry	Catalyst amount (mol%)	Temp. (°C)	[Dsim]Cl		[Msim]PF_6		[Msim]BF_4	
			Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)
1	–	110	600	32	600	29	600	30
2	5	110	8	88	14	89	17	91
3	7.5	110	5	90	9	93	10	90
4	10	110	2	98	3	98	5	97
5	10	120	3	97	6	99	6	95
6	10	100	5	92	8	90	11	91
7	10	90	9	93	11	91	12	92
8	10	80	14	90	15	89	18	87
9	15	110	3	98	6	98	7	98

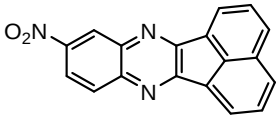
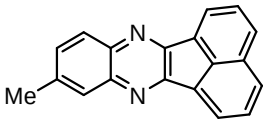
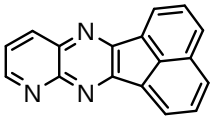
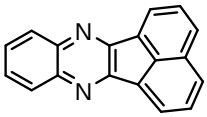
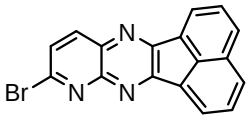
[a]Isolated yield.

1,2-Diamines was condensed with benzyl, phenanthrene-9,10-dione and acenaphthylene-1,2-dione using [Dsim]Cl, [Msim]PF_6 or [Msim]BF_4 (results summarized in **Table 2**). As it can be seen in Table 2, all catalysts were highly efficient and general, and gave the desired quinoxalines in high yields and short reaction times.

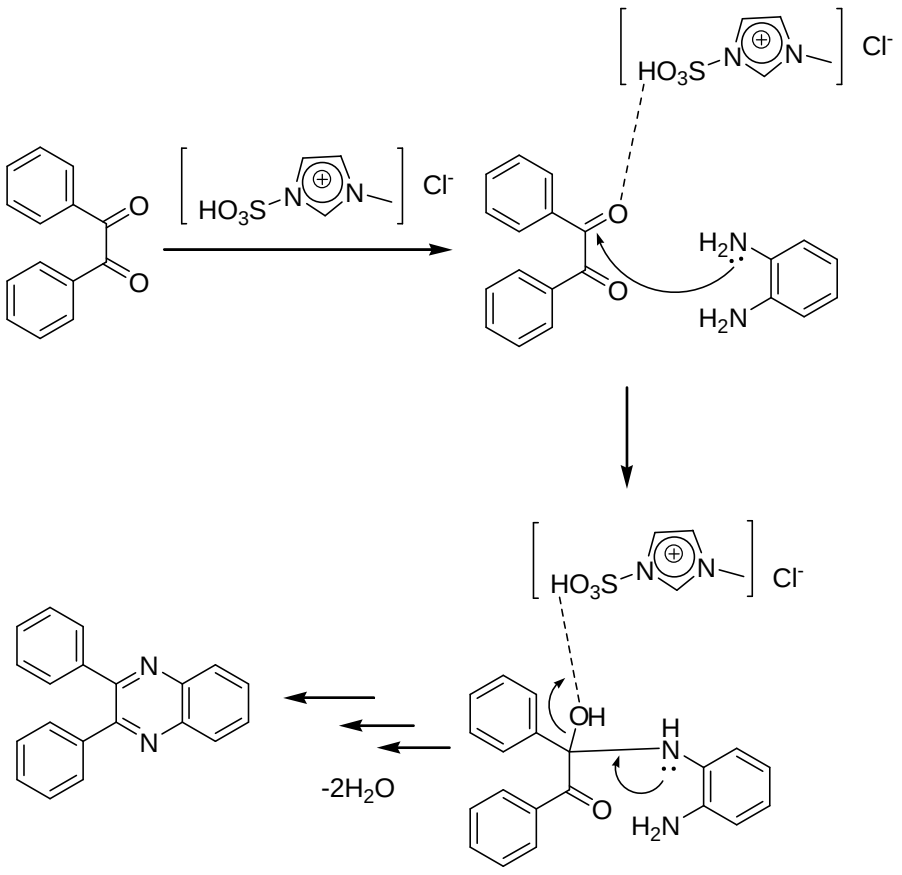
Table 2. The solvent-free synthesis of quinoxalines using the sulfonic acid functionalized imidazolium salts (SAFIS).

Entry	product[b](Q)	[Dsim]Cl		[Msim]PF_6		[Msim]BF_4		Mp °C (Lit.)
		Time (min)	Yield %	Time (min)	Yield %	Time (min)	Yield %	
1		2	98	3	98	5	97	125 - 126 128 - 129[12]
2		2	94	3	92	4	90	113 - 115 116 - 117[13]
3		20	95	25	93	30	90	127 - 128
4		15	95	18	95	30	92	140 - 142 139- 140[13]
5		25	92	30	92	30	90	185 - 186 185 - 187[13]
6		45	89	50	87	50	82	143 - 145
7		50	92	50	91	50	90	134 - 137 141 - 142[19]
8		20	91	25	89	25	89	134 - 136 148 - 150[14]
9		30	90	35	89	35	90	188 - 189 [14]
10		55	88	60	85	45	86	124 - 126

11		40	90	35	90	45	84	120 - 122
12		40	90	40	88	50	85	131 - 134
13		2	92	4	92	5	88	123 - 125 129 - 131[13]
14		15	87	18	86	25	81	145 - 147 [19]
15		2	99	3	96	3	97	225 - 226 223 - 225[13]
16		5	96	7	93	8	95	218 - 220 208 - 210[13]
17		10	98	15	91	20	94	245 - 246
18		40	86	45	91	55	84	215 - 216
19		20	94	20	90	35	89	259 - 260
20		35	91	35	90	45	90	221 - 223
21		30	94	45	93	50	90	159 - 162

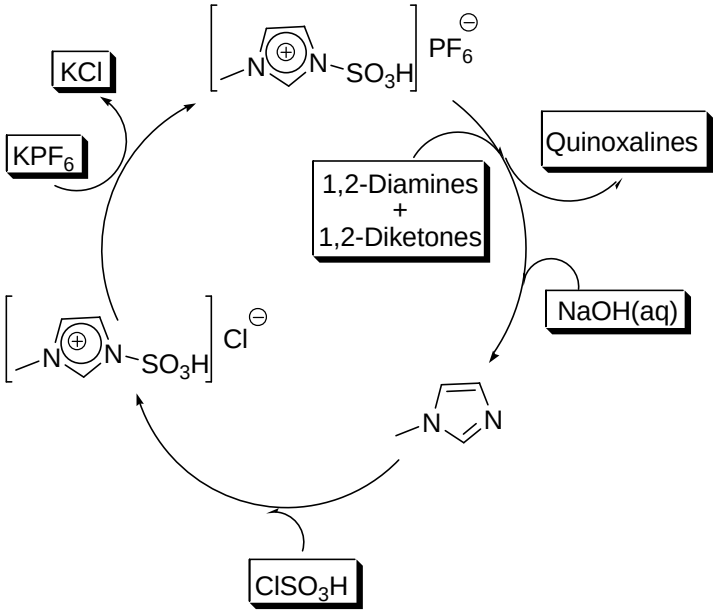
22		25	93	40	90	35	91	321-323
23		2	97	4	98	5	95	228 - 229 300[13]
24		30	93	35	90	45	88	229 - 231
25		5	91	10	90	18	90	235-236 238-240[19]
26		30	94	45	88	50	91	224-226

In a plausible mechanism (**Scheme 3**), at first, 1,2-diketone compounds is activated by the acidic group of [Dsim]Cl (or the other catalysts) to produce **I**. Then, benzene-1,2-diamines attacks to the carbonyl group of the activated 1,2-diketones, and affords intermediate **II**. Next, by removing H_2O from **II**, orthoquinone methide (*o*-QM, **III**) is prepared. [Dsim]Cl again activates intermediate **III**, afterward, by removing H_2O, 2,3-diphenylquinoxaline forms.



Scheme 3. The plausible mechanism for the condensation reaction of benzene-1,2-diamine with benzil using the [Dsim]Cl.

As previously showed, [Dsim]Cl, [Msim]PF_6 and [Msim]BF_4 were highly efficient and general for the synthesis of the quinoxaline derivatives. To raise the catalysts worth, their recoverability and reusability were studied. For this purpose, the reaction of benzene-1,2-diamine with benzil using [Msim]PF_6 was carried out several times, and the reaction mixtures were combined. Afterward, H_2O was added to the combined reaction mixtures, stirred for 5 min, and filtered [Msim]PF_6 is soluble in H_2O; however, the reaction mixture is not soluble in H_2O. In the aqueous media, a quantity of [Msim]PF_6 hydrolyzed to 1-methylimidazole (as monitored on TLC) and H_2SO_4. To complete hydrolysis of [Msim]PF_6, and consequently formation of 1-methylimidazole, a solution of NaOH (10%) was added to the filtrate, and stirred for 5 min. The solution was extracted with *t*-butylmethyl ether, washed with H_2O and dried. Evaporation of the solvent gave 1-methylimidazole. The recovered 1-methylimidazole was reacted with chlorosulfonic acid to give [Msim]Cl. [Msim]Cl was reacted with $NaPF_6$ to produce [Msim]PF_6. The catalytic activity of the reproduced [Msim]PF_6 was as same as the first one. The regeneration of this catalyst is summarized in **Scheme 4**. [Dsim]Cl and [Msim]BF_4 were also reproduced accordingly.



Scheme 4. The regeneration of [Msim]PF_6.

It should be mentioned that [Msim]Cl and [Msim]$AlCl_4$ were also successfully employed in the synthesis of the quinoxaline derivatives, and the results were similar to [Dsim]Cl, [Msim]PF_6 and [Msim]BF_4.

3. Conclusions

In summary, we have introduced some new ionic liquid of imidazolium salts including [Dsim]Cl, [Msim]PF_6 and [Msim]BF_4 as highly efficient, regenerable catalysts for organic transformations. For instance, in this work, the synthesis of quinoxalines derivatives by the one-pot condensation reaction, were efficiently catalyzed by these imidazolium salts. The promising points for the presented methodology are efficiency, generality, high yields, very short reaction times, cleaner reaction profile, simplicity, ease of preparation of the catalyst.

4. Experimental

4.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. IR spectra were run on a

Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR (500 or 300 MHz) and ^{13}C NMR (125 or 75 MHz) were run on a Bruker Avance DPX. FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Optical rotations were measured in spectral grade solvents using a Perkin–Elmer 341 polarimeter.

4.2. Preparation of ionic liquid [Msim]Cl

A round-bottomed flask (100 mL) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry CH_2Cl_2 (50 mL), and then chlorosulfonic acid (0.583 g, 5 mmol) was added dropwise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min, stand for 5 min, and the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3 × 50 mL) and dried under vacuum to give [Msim]Cl as a viscous colorless oil in 97% yield, 0.964 g[20-21].

4.3. Preparation of ionic liquids [Msim]PF_6 and [Msim]BF_4

A mixture of [Msim]Cl (0.993 g, 5 mmol) and KPF_6 (0.92 g, 5 mmol) or $NaBF_4$ (0.548 g, 5 mmol) in a round-bottomed flask (100 mL) was stirred for 12 h at 60 °**C.** Afterward, to separate produced ionic liquid from KCl or NaCl, absolute ethanol (25 mL) was added to the reaction mixture, stirred for 2 min, and filtered (KCl and NaCl are insoluble in absolute ethanol). The solvent of the filtrate was evaporated under vacuum to give [Msim]PF_6 or [Msim]BF_4 in 92% (1.421 g) and 94% (1.173 g) yields, respectively.

4.4. Spectral data of [Msim]PF_6 and [Msim]BF_4

4.4.1. 3-Methyl-1-sulfonic acid imidazolium hexafluorophosphate(V) {[Msim]PF_6}

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.82 (s, 3H, CH_3), 7.55 (s, 2H), 8.90 (s, 1H), 14.15 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 35.6, 119.9, 123.4, 136.0; CHN Analysis: Anal. Calcd for $C_4H_7F_6N_2O_3PS$: C, 15.59; H, 2.29; N, 9.09. Found: C, 15.67; H, 2.37; N, 8.94; MS: *m/z* = 309 (M^+ + 1), 308 (M^+), 163 (M^+-PF_6), 293 (M^+-CH_3), 227 (M^+-SO_3H); ^{31}P NMR (121 MHz, DMSO-d_6): −143.7 (septet, ^{1}J (P,F) = 711 Hz, PF_6^-).

4.4.2. 3-Methyl-1-sulfonic acid imidazolium tetrafluoroborate {[Msim]BF_4}

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.83 (s, 3H, CH_3), 7.51 (s, 1H), 7.56 (s, 1H), 8.89 (s, 1H), 14.05 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 35.7, 119.9, 123.5, 135.9; CHN Analysis: Anal. Calcd for $C_4H_7BF_4N_2O_3S$: C, 19.22; H, 2.82; N, 11.21. Found: C, 18.97; H, 2.94; N, 11.03; MS: *m/z* = 251 (M^+ + 1), 250 (M^+), 163 (M^+-BF_4), 235 (M^+-CH_3), 169 (M^+-SO_3H).

4.5. General procedure of preparation of quinoxalines

A mixture of aromatic o-diamine (1mmol), 1,2-dicarbonyl compound (1mmol), aldehyde (1 mmol) and ionic liquid (0.1 mmol) in a 10 mL round-bottomed flask connected to a reflux condenser, was stirred in an oil-bath (110 ^{o}C). After completion of the reaction, as monitored with TLC, the reaction mixture was cooled to room temperature, H_2O (20 mL) was added to it, stirred for 25 min to remove ionic liquid, filtered and dried. The crude product was recrystallised from hot ethanol to afford the pure product.

4.6. Selected specteral data of quinoxalines

4.6.1. 2,3-Diphenylquinoxaline(1Q)

white solid, FT-IR (KBr): 1556 cm^{-1}; ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm7.33977(bs, 6H, Ar-H) 7.54183(bs, 4H, Ar-H) 7.74584(bs, 2H, Ar-H) 8.20007(bs, 2H, Ar-H) ; ^{13}C NMR (300 MHz, $CDCl_3$): 128.290, 128.896, 129.121, 129.913, 130.066, 138.921, 141.115, 153.384; MS: *m/z* = 282 (M+).

*4.6.2. 6-Methyl-2,3-diphenylquinoxaline(***2Q)**

brown solid, FT-IR (KBr): 1619 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 2.61(s, 3H, Ar-CH_3) 7.35(s, 6H, Ar-H) 7.55(d, J=6.48, 4H, Ar-H)7.60(s, 1H, Ar-H) 7.98(s, 1H, Ar-H) 8.09(d, J=8.4, 1H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 21.948, 128.040, 128.244, 128.663, 128.731, 129.903, 129.915, 132.321, 139.246, 139.728, 140.486, 141.289, 152.552, 153.289; MS: *m/z* = 296 (M+).

*4.6.3. 6-Nitro-2,3-diphenylquinoxaline(***5Q***)*

red solid, FT-IR (KBr): 1656 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 7.38(bs, 6H, Ar-H) 7.56(bs, 4H, Ar-H) 8.28(bs, 1H, Ar-H) 8.45(bs, 1H, Ar-H) 9.02(bs, 1H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$):; MS: 123.269, 125.512, 128.450, 129.667, 129.854, 129.953, 130.666, 137..950, 139.870, 143.390, 147.801, 155.621, 156.176; MS: *m/z* = 327 (M+).

*4.6.4. 2,3-bis(4-Methoxyphenyl)quinoxaline(***8Q***)*

yellow solid, FT-IR (KBr): 1615 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 3.85(s, 6H, $2_{\times}CH_3$) 6.87(d, J=7.77, 1H, Ar-H) 6.94 (d, J=7.77, 4H, Ar-H) 7.50 (d, J=7.14, 1H, Ar-H) 7.71(s, 1H, Ar-H) 7.93(d, J=7.62, 4H, Ar-H) 8.13(s, 1H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 55.291, 55.615, 113.786, 114.300, 126.271, 128.875, 129.645, 131.307, 131.449, 132.315, 140.867, 152.926, 160.267, 164.867, 193.506; MS: *m/z* = 342 (M+).

*4.6.5. Dibenzo[a,c]phenazine(***15Q***)*

yellow solid, FT-IR (KBr): 1604 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 7.71(s, 4H, Ar-H) 7.85(s, 2H, Ar-H) 8.35(s, 2H, Ar-H) 8.43(s, 2H, Ar-H) 9.33(s, 2H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 122.875, 126.448, 128.023, 128.925, 129.356, 130.205, 130.661, 132.019, 141.323, 141.876; MS: *m/z* = 280 (M+).

*4.6.6. 11-Methyl-dibenzo[a,c]phenazine(***16Q***)*

brown solid, FT-IR (KBr): 1624 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 2.65(s, 3H, CH_3) 7.72(bs, 5H, Ar-H) 8.04(s, 1H, Ar-H) 8.15(s, 1H, Ar-H) 8.47(s, 2H, Ar-H) 9.32(bs, 2H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 20.058, 122.795, 126.032, 126.178, 127.793, 128.797, 129.978, 130.127, 131.727, 131.922, 132.368, 140.393, 140.573, 141.508, 141.971; MS: *m/z* = 294 (M+).

*4.6.7. 11-Benzoil-dibenzo[a,c]phenazine(***17Q***)*

yellow solid, FT-IR (KBr): 1653, 1606 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 7.27(s, 1H, Ar-H) 7.60(s, 2H, Ar-H) 7.71(s, 2H, Ar-H) 7.79(s, 2H, Ar-H) 7.98(s, 2H, Ar-H) 8.35(s, 1H, Ar-H) 8.52(s, 3H, Ar-H) 8.69(s, 1H, Ar-H) 9.31(s, 1H, Ar-H) 9.44(s, 1H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 123.048, 128.254, 128.601, 129.450, 130.220, 130.754, 131.056, 132, 916, 140.540, 140.980, 141.323, 141.876, 154.046; MS: *m/z* = 384 (M+).

*4.6.8. 2-Bromopyrido-[2,3-b]dibenzo[5,6-7,8]quinoxalines (***18Q***)*

yellow solid, FT-IR (KBr): 1603 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 7.72(bs, 4H, Ar-H) 8.41(bs, 2H, Ar-H) 8.66(s, 1H, Ar-H) 9.06(s, 1H, Ar-H) 9.12(s, 1H, Ar-H) 9.30(s, 1H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 122.858, 126.519, 127.292, 128.048, 129.026, 131.393, 139.507, 143.815, 155.170; MS: *m/z* = 360 (MH+).

*4.6.9. 9-Methylacenaphto[1,2-b]quinoxaline(***23Q***)*

Brown solid, FT-IR (KBr): 1626 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 2.56(s, 3H, CH_3) 7.49(d, J=8.31, 1H, Ar-H) 7.70(t, J=7.5, 2H, Ar-H) 7.88(s, 1H, Ar-H) 7.94(d, J=8.07, 2H, Ar-H) 7.99(d, J=8.61, 1H, Ar-H) 8.27(t, J=6.40, 2H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 21.735, 121.583, 121.785, 128.484, 128.554, 128.938, 129.113, 129.284, 129.799, 131.250, 131.645, 136.097, 139.359, 139.666, 140.915, 153.035, 153.661; MS: *m/z* = 268 (M+).

*4.6.10. Acenaphto[1,2-b]quinoxaline(***25Q***)*

Yellow solid, FT-IR (KBr): 1614 cm^{-1}(stretching C=N); ^{1}H-NMR (FT-300 MHz, $CDCl_3$/TMS): dppm 7.74-7.81(m, 4H, Ar-H) 8.05(d, J=8.16, 2H, Ar-H) 8.20-8.23(m, 2H, Ar-H) 8.4(d, J=6.87, 2H, Ar-H); ^{13}C NMR (300 MHz, $CDCl_3$): 122.328, 128.679, 129.285, 129.442, 129.694, 129.900, 131.248, 136.479, 140.707, 153.595; MS: *m/z* = 254 (M+).

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