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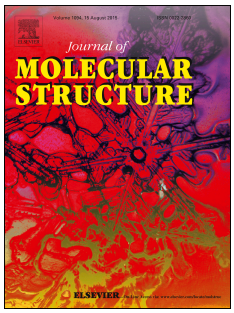

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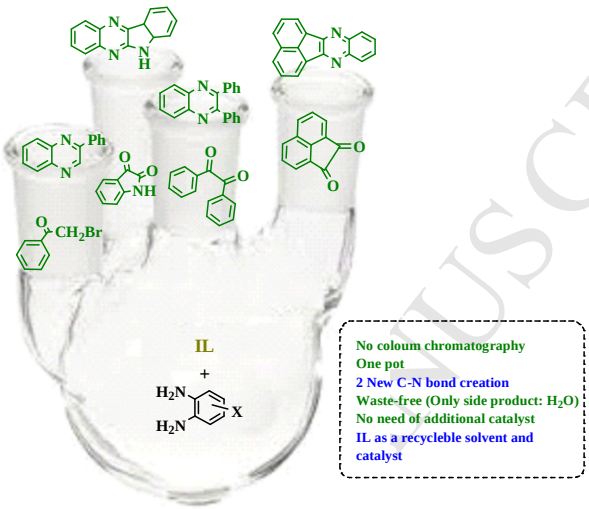
Graphical Abstract



An environmentally benign attribute for the expeditious synthesis of quinoxaline derivatives

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ABSTRACT

A simple, efficient, and environmentally friendly ionic liquid mediated protocol for the synthesis of quinoxaline derivatives using carbonyl substrate and phenylenediamines has been described. A range of ionic liquids were synthesized, characterized *via* IR, ^{1}H and ^{13}C NMR and used as a solvent as well as catalyst for above protocol. The catalytic activities of ILs were evaluated and the relationship between the catalytic activity and acidity was discussed. It was also found that among the all ILs, $[Bmim]CF_3SO_3$ was the most effective, eco-friendly and less expensive solvent and catalyst for the above etiquette. This method is of significant value due to the eco-friendly nature of ionic liquid and non usage of separate catalyst to drive the reaction forward. The protocol proves to be efficient and environmentally benign in terms of good to excellent yields, low reaction times, simple work-up, ease of recovery, and reusability of ionic liquid for six times.

KEYWORDS: Ionic liquids, Quinoxalines, Reusable media, Reusable catalyst

1. INTRODUCTION

Owing to the growing emphasis on the desire to develop more sustainable routes for the preparation of a myriad of materials, green chemistry and sustainability are becoming increasingly important in organic synthesis [1]. Solvents constitute around 80% of the total volume of chemicals used in a process [2]. Separation, purification and recycling of solvents is a very important criteria that directly affects the eco-efficiency of a process and thus its industrial viability [3]. However majority of solvents used in chemical laboratories and industries are organic chemicals with hazardous and toxic properties and form part of the large waste by-products causing environmental hazards [4]. Although most of their toxic potential is known and there are safety measures for their use, prolonged and high concentration exposures can adversely affect respiratory, hematological and thyroid functioning [5]. Thus careful selection of solvents is important not only for increasing the reaction rates and lowering the reaction temperatures but also for the sustainable development of the environment. One such approach to enhance the eco compatibility of a reaction is to conduct it in green solvents instead of classical organic solvents and devise more efficient recycling protocols [6]. In the last decade, many promising media have appeared as inoffensive solvents, such as water, supercritical fluids, and perfluorinated solvents [7]. However, the use of these solvents is still limited by many problems: some substrates or reagents have a poor solubility or stability in water; sophisticated equipment is usually required when perfluorinated or supercritical solvents are employed.

This has initiated tremendous interest in the use of ionic liquids for practical implementation as green solvents [8-9]. Ionic liquids have certainly appeared to be ace in the sleeve of green chemistry, as they offer the promise of being simultaneously environmentally benign while hosting an array of materials for unique chemistry [10-12]. They possess several unconventional and distinctive properties such as negligible vapor pressure, wide liquid range, low flammability, high conductivity, excellent thermal stability etc [13-14].

Quinoxalines are an important class of heterocycles found in many pharmacologically and biologically active molecules (Fig.1). It has wide applications such as antiviral, antibacterial, antiinflamatory, anticonvulsant, anticancer, anti HIV and as kinase inhibitor [15-17]. Moreover, they are widely used in the field of semiconductors, dyes, suitable ligands in coordination chemistry electroluminescent material and in chemically controllable switches [18-20].

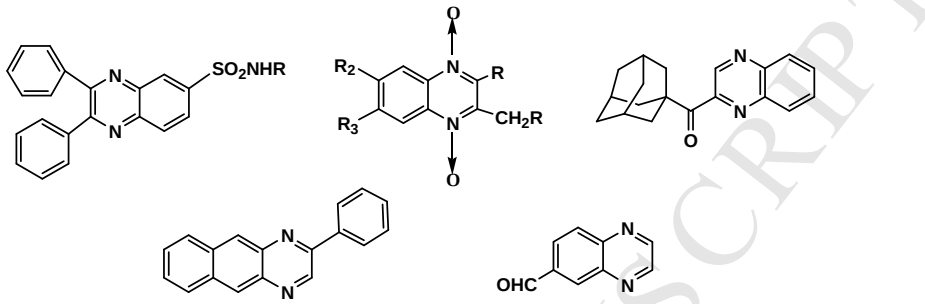
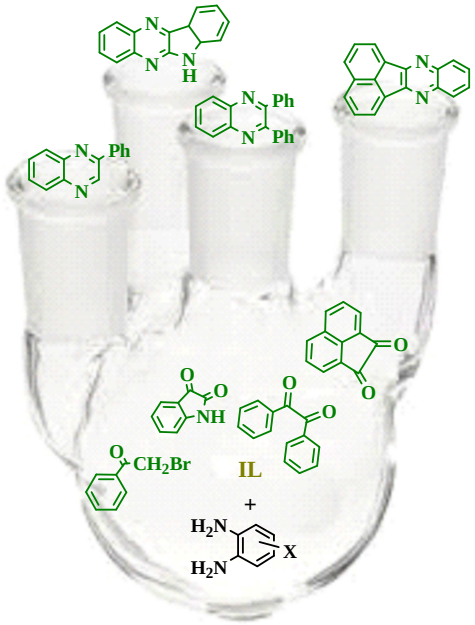


Fig. 1. Representatives of quinoxaline containing compounds.

Consequently a number of synthetic strategies have been devised for the synthesis of various substituted quinoxalines. Commonly a highly efficient method comprises the reaction of aryl 1,2-diamines with carbonyl compounds. Usually this condensation reaction is carried out under reflux condition in ethanol or acetic acid [21]. However in recent years several new feasible methods have been developed including the use of β-cyclodextrins, iodine, $MnCl_2$, heteropolyacids, montmorillonite, Zn[(L)-PROLINE], polyaniline sulphate salts, DABCO, fluorinated alcohols and alumina supported heteropolyoxometallates [22-26]. While, some deliberately sound improvisation have been documented [27-29] for upliftment of reaction condition, but somewhere down the line it still require the adaptability due to the use of expensive and/or toxic catalysts, incompatibility with certain functional groups, critical product isolation procedures, expensive reagents and limited substrate applicability.

Therefore the necessecity of designing a synthetic protocol which abides the principles of green chemistry remains an attractive goal. To circumvent the above drawbacks and develop a simple, efficient and green route for the synthesis of quinoxaline, herein, we describe dual catalytic-solvent system role of ionic liquid as a green solvent as well as catalyst for the synthesis of quinoxaline derivatives via reaction of 1,2-diamine with different carbonyl substrates at room temperature. As shown in Scheme 1, various aromatic aldehydes, cyclic ketones, heterocyclic ketones and phenacyl bromides were used as starting materials. ILs were employed as solvents and catalysts at room temperature. The catalytic activities of ILs were evaluated and the relationship between the catalytic activity and acidity was discussed. It was also found that the [Bmim]CF_3SO_3 was the most effective catalyst and solvent for this protocol. Additionally, this IL is more eco-friendly and less expensive as compared to other ILs.



Scheme 1: Synthesis of quinoxaline derivatives

2. EXPERIMENTAL

2.1 Chemicals and Apparatus:

All the chemicals used were of research grade (purchased from Sigma Aldrich and Acros) and used without further purification. The melting points of all compounds were determined on a Toshniwal apparatus in capillary and uncorrected. IR spectra were recorded on a Shimadzu FT IR- 8400S spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using $CDCl_3$ as solvent on a JEOL JNM LA-300 spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR). The ^{1}H NMR data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm), chemical shift (multiplicity, coupling constant in Hz, integration), and the ^{13}C NMR data in ppm (δ) from the internal standard (TMS, 0.0 ppm). Mass spectra were obtained using Waters Xevo G_2S instrument.

2.2 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 all the reactions was confirmed by ^{1}H and ^{13}C NMR. The crude product was used without further purification for the next step, the anion metathesis.

2.3 General procedure for anion metathesis:

To a solution of the crude 1-butyl-3-methylimidazoliumbromide, obtained from the above reactions, 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. Same procedure was used except that trifluoro methane sulphonic acid (15.08 g, 100.0 mmol) was used instead of hexafluorophosphoric acid. The resulting mixture was filtered. Evaporation of the solvent under reduced pressure afforded the corresponding imidazolium trifluromethane sulphonate.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 ^{1}H NMR.

2.4 General procedure for the synthesis of Quinoxalines:

A mixture of aromatic diamine derivatives (2 mmol) and a 1,2- dicarbonyl compound (2 mmol) in ionic liquid (2 mL) was stirred at room temperature for the appropriate time. The progress of the reaction was monitored by TLC (*n*-Hexane: EtOAc, 7:3), after completion of the reaction, the reaction mixture was diluted with water and extracted using diethyl ether (30ml). The combined organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure to afford the corresponding product. The residual ionic liquid was dried under vacuum and reused. The same procedure was repeated for the reaction of aromatic anilines with isatin and acenaphthoquinone and phenaacyl bromide. All the products obtained were characetrised by IR, ^{1}HNMR, ^{13}CNMR and Mass studies.

2.5 Spectral data of [Bmim]CF_3SO_3 ionic liquid

1-Butyl-3-methylimidazolium trifluoromethanesulphonate:

IR (cm^{-1}): 1175, 1468, 1581, 1630, 2884, 2935, 2970, 3140, 3180, 3647. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.803 (t, 3H, CH_3, J = 7.2Hz), 1.15-1.23(m, 2H, CH_2), 1.65-1.75 (m, 2H, CH_2), 3.80 (s, 3H, CH_3), 4.02-4.07 (m, 2H,CH_2), 7.32 (dd, 2H, ArH, J=1.2Hz), 8.816 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$,75 MHz): 12.9, 19.0, 31.7, 36.0, 49.5, 114.1, 118.3, 122.9, 126.0, 136.1.

2.6 Spectral data of representative quinoxalines:

2,3-Diphenylquinoxaline (**3a**)*:* Mp 123-125 °C; ^{1}H NMR(300 MHz, $CDCl_3$) δ: 7.32-7.39 (m, 6H, ArH), 7.52-7.54 (m, 4H, ArH), 7.71-8.26 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 127.1, 127.5, 128.1, 128.8, 129.4, 138.4, 142.6, 154.4. MS (ESI) m/z: 283.19 $[M+H]^+$.

9-Methyl-6*H*-indolo[2,3-*b*]quinoxaline, (**4c**) Mp 295-297 °C; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 1.03 (s, 3H, CH_3), 7.40-7.48 (m, 2H, ArH), 7.64-7.80 (m, 2H, ArH), 8.01-8.08 (m, 2H, ArH), 8.21-8.25 (m, 1H, ArH), 11.21 (s, 1H, NH). ^{13}C NMR (DMSO-d_6,75 MHz) δ: 20.8 110.7 , 116.2, 118.7, 122.8, 124.6, 126.3, 128.7, 128.9, 129.2, 131.3, 137.3, 139.7, 141.8, 146.4. MS (ESI) m/z: 234 $[M+H]^+$.

9-Methyl-acenaphtho[1,2-b]quinoxaline (5b) Mp 208-210 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.87 (s, 3H, CH_3), 7.18-8.37 (m. 9H, ArH).^{13}C NMR ($CDCl_3$,75MHz) δ:17.5, 121.7, 127.4, 128.5, 128.8, 129.2, 129.3,129.5, 130.0, 132.1, 132.4, 138.0, 141.3. MS (ESI) m/z: 269.31 $[M+H]^+$.

5-Methyl-2-*p*-tolyl-quinoxaline (6g) Mp 109-111 °C; ^{1}HNMR ($CDCl_3$ 300 MHz) δ: 2.38 (s, 3H, CH_3), 2.81 (s, 3H, CH_3), 7.18-9.25 (m, 8H, ArH). ^{13}CNMR ($CDCl_3$,75MHz) δ: 21.45, 29.71, 127.2, 127.3, 127.5, 129.6, 129.9, 130.2, 130.4,133.7 137.2, 140.5, 141.5, 141.8, 151.2. MS (ESI) m/z: 235.19 $[M+H]^+$.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of ionic liquids

In order to exploit the potential of ionic liquids for the synthesis of quinoxaline derivatives, we first carried out the one-pot synthesis of three different ionic liquids (Fig. 2), [Bmim]BF_4, [Bmim]CF_3SO_3, [Bmim]PF_6 using 1-methylimidazole and various alkyl halides as the starting materials [30]. FR-IR spectra in the 2800–3200 cm^{-1} show the CH_x stretching region of the pure ILs. For pure [Bmim] CF_3SO_3, the bands at around 3140 cm^{-1} and 3180 cm^{-1} are attributed to the *ν*(C2–H) and *ν*(C4,5–H) of the imidazolium ring respectively, while the bands in the range of 3000–2800 cm^{-1} are originated from the butyl chain attached to the imidazolium ring. As these ILs ([Bmim]BF_4, [Bmim]CF_3SO_3, [Bmim]PF_6) all share the common $[Bmim]^+$ cation where the CH_x resides structurally, the large differences in the IR spectra are unusual and intriguing. The ^{1}H NMR spectrum, closely resembled to that of imidazolium ring structure of ILs. For pure [Bmim] CF_3SO_3, the peak at δ 8.81 can be assigned as the C(2)–H proton The chemical shift of the C(4,5)–H protons of imidazolium ring appears at δ 7.32. The characteristic signals with appropriate chemical shift and coupling constant for the twelve protons show the presence of alkyl chain attached to the imidazolium ring. In these ILs, the much smaller shifts for C(2,4,5)–H are noticeable, confirming that the hydrogen bonding is much weaker. In addition to this, the chemical shifts do not show much difference between C(2)–H and C(4,5)–H, suggesting a less specific hydrogen bonding.

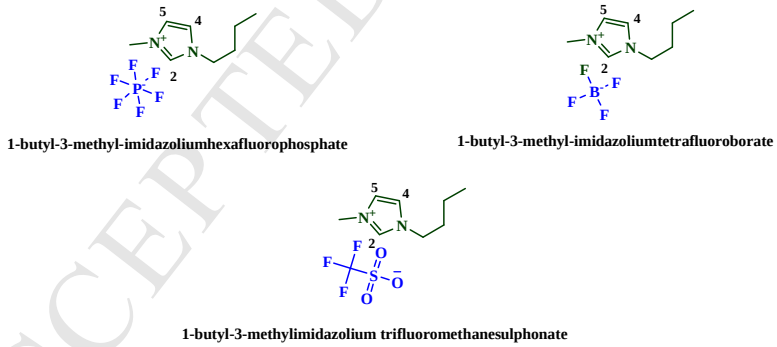


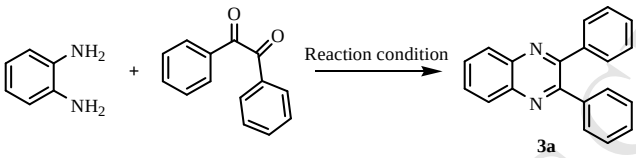
Fig. 2. Structure of synthesized Ionic Liquids

3.2 Optimization of reaction conditions

With the aim of optimizing the reaction conditions the condensation reaction of 1,2-phenylene diamines with benzyl was employed as a model reaction. In subsequent investigations the model reaction was carried out in different solvents and the results have been summarized in Table1. It can be concluded that polar solvents gave better yields than non-polar solvents. Poor yield was observed on using toluene (non-polar) as a solvent and small increase was observed when chlorinated solvents like DCM and $CHCl_3$ were used. The small increase in product yield was observed on using ethyl acetate, ethanol, water and acetic acid due to the progressive increase in the polarity of the

solvent. The reaction was then carried out using various ILs as both catalyst and solvent (Table 1). On using [Bmim]BF_4 as the solvent, moderate amount of product was obtained. On diverging from [Bmim]PF_6 to [Bmim]CF_3SO_3 the product yield changed from good to excellent. On evaluating all these solvents [Bmim]CF_3SO_3 came out as the solvent of choice as it afforded the product in excellent yield and no hazardous by products were obtained.

Table 1: Effect of solvent on the synthesis of quinoxaline derivatives (3a)[a].



3a

Entry	Solvent	Time	Yield (%)*
1.	Toluene	24 h	12
2.	DCM	9 h	14
3.	$CHCl_3$	4 h	16
4.	Ethyl Acetate	2.5 h	22
5.	Ethanol	2 h	26
6.	Water	2.5 h	32
7.	Acetic Acid	2 h	38
8.	[Bmim]BF_4	20 min	88
9.	[Bmim]PF_6	15 min	91
10.	[Bmim]CF_3SO_3	10 min	96

[a]All reactions were carried out using benzil (2 mmol), ortho-phenylenediamine (2 mmol) at room temperature.
* Isolated yield.

The above results demonstrate that the activities of the ILs depend on both their cations and anions and the anion counterparts of the ILs appear to affect the reaction more significantly. The efficacy of the IL to promote the reactions was correlated with the basicity of the anions. It can be assumed that the nature of the anion would govern the electrophilicity of the imidazolium cation which in turn has a bearing on the acidity of the ILs. It was observed that with increasing basicity of the anion there is a progressive increase in yield which is due to an increase in the acidity of the IL [31].

In order to prove the catalytic activity of the IL [Bmim]CF_3SO_3 for this reaction, controlled experiments employing catalytic amounts of the IL for the reaction were conducted using THF as the solvent, and the results are presented in Table 2. No product was formed when the reaction was carried out in the absence of the IL, while the reaction

occurred as the IL was added into the solvent, and the yield of product increased with the increased amount of the IL, demonstrating that the IL was an active catalyst for the reaction. Therefore, it could be concluded that the IL acted as both solvent and catalyst for the reaction.

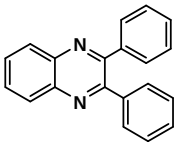
Table 2: Synthesis of quinoxaline derivatives in THF with and without [Bmim]CF_3SO_3[a]

Entry	[Bmim]CF_3SO_3 (mol%)	Solvent	Yield (%)*
1.	0	THF	0
2.	10	THF	38
3.	50	THF	68

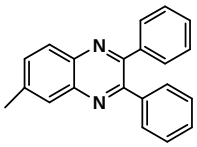
[a]All reactions were carried out using benzil (2 mmol), ortho-phenylenediamine (2 mmol) in 2ml THF at room temperature.
* Isolated yield.

The general efficiency of this protocol was than studied for the synthesis of a variety of quinoxalines and the results are shown in Table 3. It can be inferred that this reaction offers a wide substrate scope, a series of aromatic diamines with both electron donating and electron withdrawing substituent reacted with benzil under the optimized reaction conditions. The presence of an electron donating group at the phenyl ring of aromatic diamines favoured the formation of products. In contrast electron withdrawing groups such as chloro and bromo gave slightly lower yield.

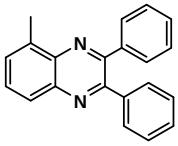
To further explore the potential of this protocol we investigated the reaction of 1,2-phenylenediamine with isatin, acenaphthoquinone and phenacyl bromide. All the reactions proceeded smoothly with high efficiency and it was observed that the change in electrophilicity of the substituents on carbonyl compounds did not significantly affect the yield of product. The present method should be applicable to the synthesis of libraries with high diversity. We expect this method to find extensive application in the field of combinatorial chemistry, diversity-oriented synthesis, and drug discovery. The structures of the products were established by IR, ^1H, ^{13}C NMR and Mass studies.



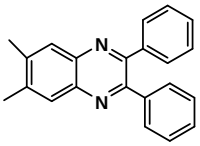
3a, 15 min., 95%
M.P.=123-125 [32][a]



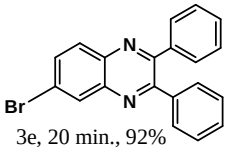
3b, 12 min., 96%
M.P.=118-120 [32][a]



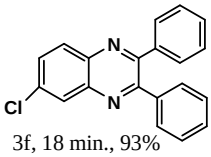
3c, 10 min., 97%
M.P.=98-101



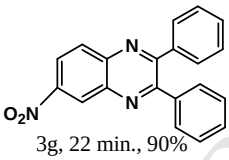
3d, 10 min., 97%
M.P.=170-171 [33][a]



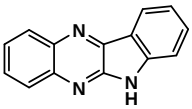
3e, 20 min., 92%
M.P.=115-117 [34][a]



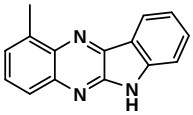
3f, 18 min., 93%
M.P.=118-119 [34] [a]



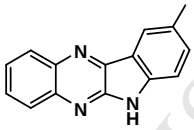
3g, 22 min., 90%
M.P.=186-188 [32] [a]



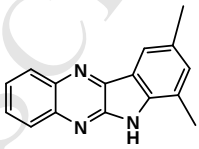
4a, 10 min., 95%
M.P.=294-296 [35][a]



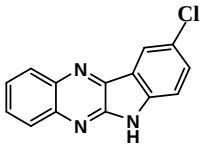
4b,10 min., 95%
M.P.=247-249



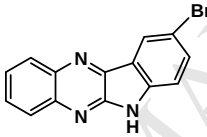
4c, 11 min., 94%
M.P.=295-297 [35][a]



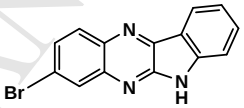
4d, 14 min., 92%
M.P.= >300 [36][a]



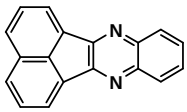
4e, 10 min., 97%
M.P.=286-289 [37][a]



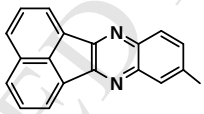
4f, 10 min., 96%
M.P.=287-289 [37][a]



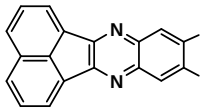
4g, 10 min., 96%
M.P.=180-182



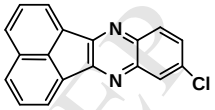
5a,15 min., 95%
M.P.=240-242 [38][a]



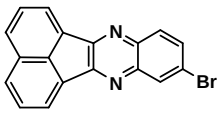
5b,10 min., 96%
M.P.=208-210 [38][a]



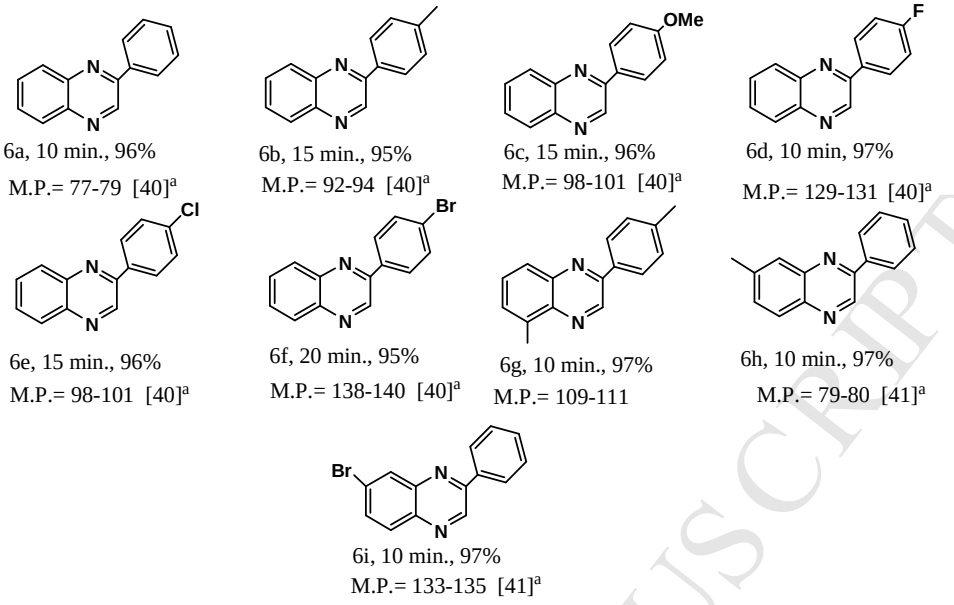
5c,10 min., 96%
M.P.= >300 [39][a]



5d, 15 min., 93%
M.P.= 224-226 [38][a]



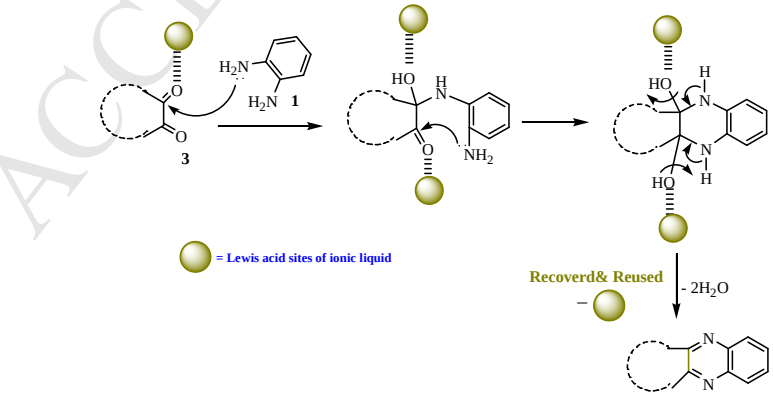
5e, 20 min., 91%
M.P.= 238-240



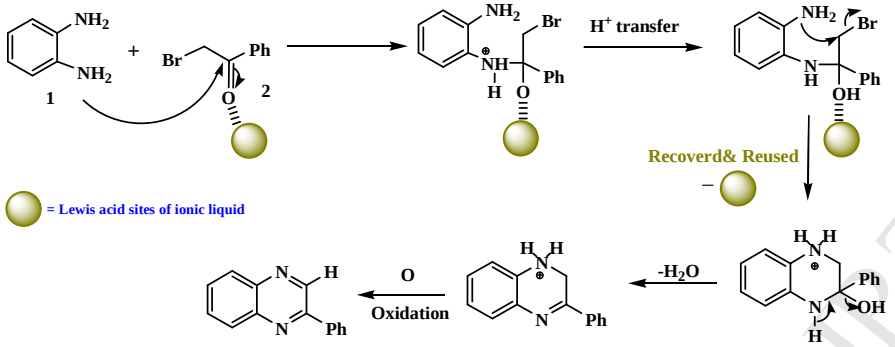
[a] Reported ref.

Table 3. Diversity of quinoxaline derivatives.

A plausible mechanism for the [Bmim]CF_3SO_3 catalyzed formation of quinoxaline is proposed as depicted in Scheme 2 and 3. The Lewis acidic site present in ionic liquid interacts with both the carbonyl oxygens of 1,2-diketo compounds respectively, as given in Scheme 2, which increases the electrophilic character of carbonyl carbon. Due to these interactions, initial addition of ortho-phenylenes with 1,2-diketo compounds give an amino-1,2-diol. The resultant amino-1,2-diol undergoes dehydration to give quinoxaline **3a-g, 4a-g, 5a-e** as the end product. Similarly, Lewis acidic sites of ionic liquid were coordinated to the oxygen of carbonyl group of phenacyl bromide and induce electrophilic activation of carbonyl carbon, which benefits the nucleophilic attack of one of the amines from ortho-phenylene on active carbonyl group. Subsequently, the nucleophilic attack of another amine group from ortho-phenylene on carbonyl carbon and followed by water elimination and a following oxidation to yield the desired product of quinoxaline derivative **6a-i** (Scheme 3).



Scheme 2. Plausible mechanism for the synthesis fused quinoxaline derivatives.



Scheme 3. Plausible mechanism for the synthesis of 2- substituted quinoxaline derivatives.

3.3 Recyclability of ILs

To examine the recyclability of ionic liquids, on completion of the reaction the mixture was filtered to separate the product. After washing the IL with the appropriate solvent (diethyl ether),it was subjected to distillation at 80 ^{0}C under reduced pressure for one hour to remove the solvent and leaving behind the IL in complete recovery. The recovered IL was further used for a series of reaction cycles (at least six times) without considerable loss in yield and purity of the product (Fig. 3).

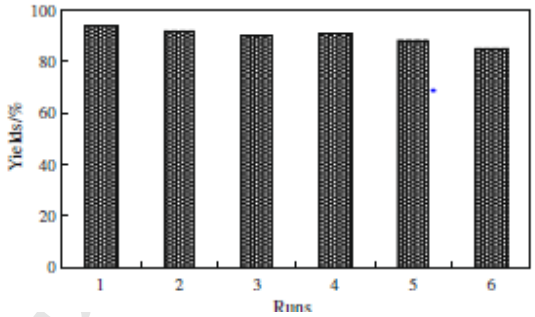


Fig. 3. Recyclability of IL for the synthesis of quinoxaline

4. CONCLUSION

In conclusion, a series of efficient and sustainable ionic liquids as green solvents were prepared and employed for the synthesis of quinoxaline derivatives via the condensation of carbonyl compounds with aromatic diamines in relatively high yields at room temperature. High yields, greenness, recyclability of the ionic liquids with no loss in its activity, operational simplicity and wide substrate scope are the important features of this new protocol. Furthermore, the present procedure is readily amenable to parallel synthesis and generation of combinatorial substituted quinoxaline libraries.

5. ACKNOWLEDGMENTS

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6. SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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Supporting Information

Contents: **Page No.**

1. General

Chemicals and Apparatus:

All the chemicals used were of research grade (purchased from Sigma Aldrich and Acros) and used without further purification. The melting points of all compounds were determined on a Toshniwal apparatus in capillary and uncorrected. IR spectra were recorded on a Shimadzu FT IR- 8400S spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using $CDCl_3$ as solvent on a JEOL JNM LA-300 spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR). The ^{1}H NMR data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm), chemical shift (multiplicity, coupling constant in Hz, integration), and the ^{13}C NMR data in ppm (δ) from the internal standard (TMS, 0.0 ppm). Mass spectra were obtained using Waters Xevo G_2S instrument.

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 0^0C. The reaction mixture was stirred for 24-48 h at 30 ^{0}C. Removal of the solvent under reduced pressure afforded crude 1-butyl-3- methylimidazolium bromide. Completion of all the reactions was confirmed by ^{1}H and ^{13}C 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-methylimidazoliumbromide, obtained from the above reactions, 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. Same procedure was used except that trifluoro methane sulphonic acid (15.08 g, 100.0 mmol) was used instead

of hexafluorophosphoric acid. The resulting mixture was filtered. Evaporation of the solvent under reduced pressure afforded the corresponding imidazolium trifluromethane sulphonate.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 ^{1}H NMR.

General procedure for the synthesis of Quinoxalines:

A mixture of aromatic diamine derivatives (2 mmol) and a 1,2- dicarbonyl compound (2 mmol) in ionic liquid (2 mL) was stirred at room temperature for the appropriate time. The progress of the reaction was monitored by TLC (*n*-Hexane: EtOAc, 7:3), after completion of the reaction, the reaction mixture was diluted with water and extracted using diethyl ether (3x10ml). The combined organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure to afford the corresponding product. The residual ionic liquid was dried under vacuum and reused. The same procedure was repeated for the reaction of aromatic anilines with isatin and acenaphthoquinone and phenaacyl bromide. All the products obtained were characetrised by IR, ^{1}HNMR, ^{13}CNMR and Mass studies.

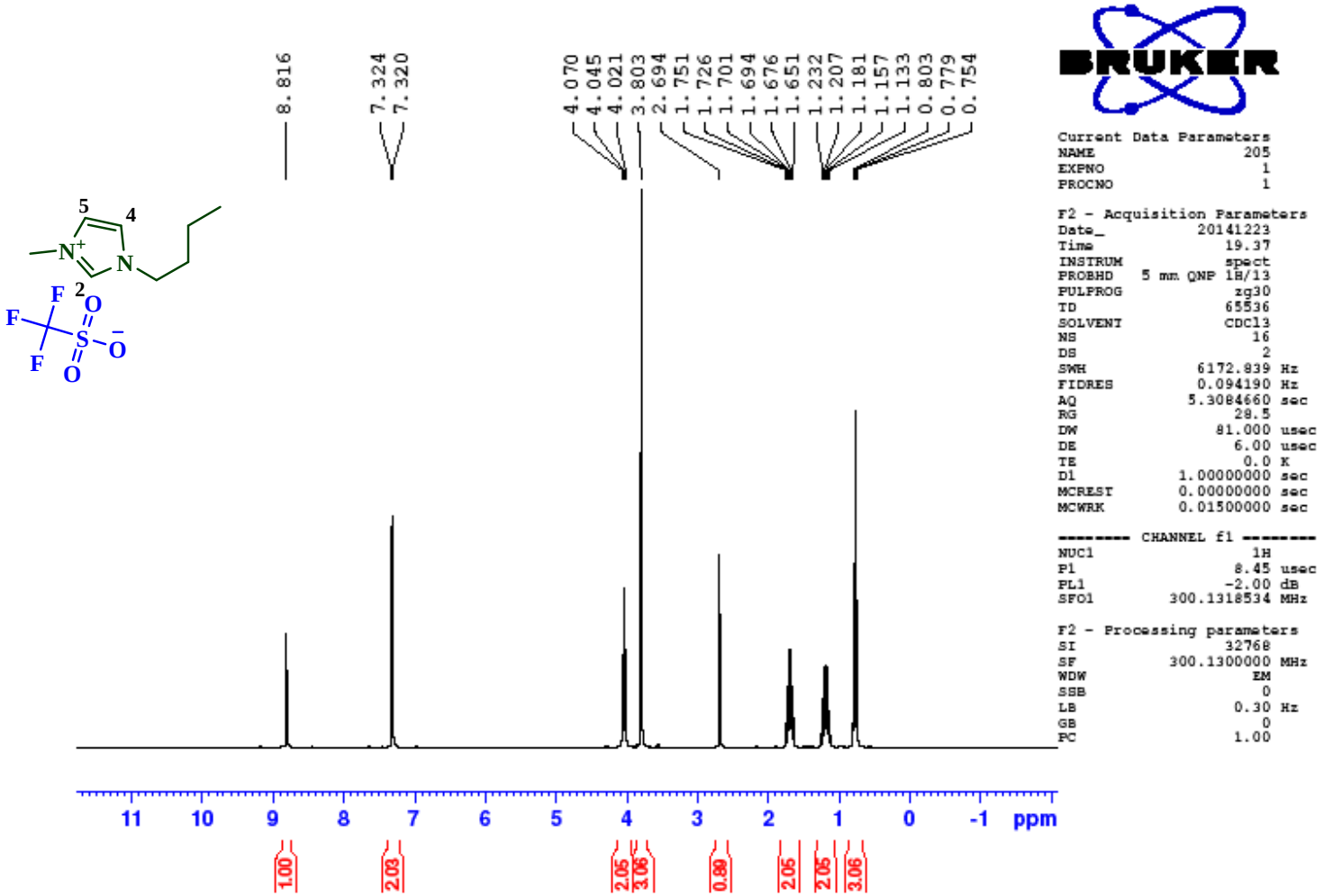

Fig. 1: ^{1}H NMR spectrum of **[Bmim]CF_3SO_3**

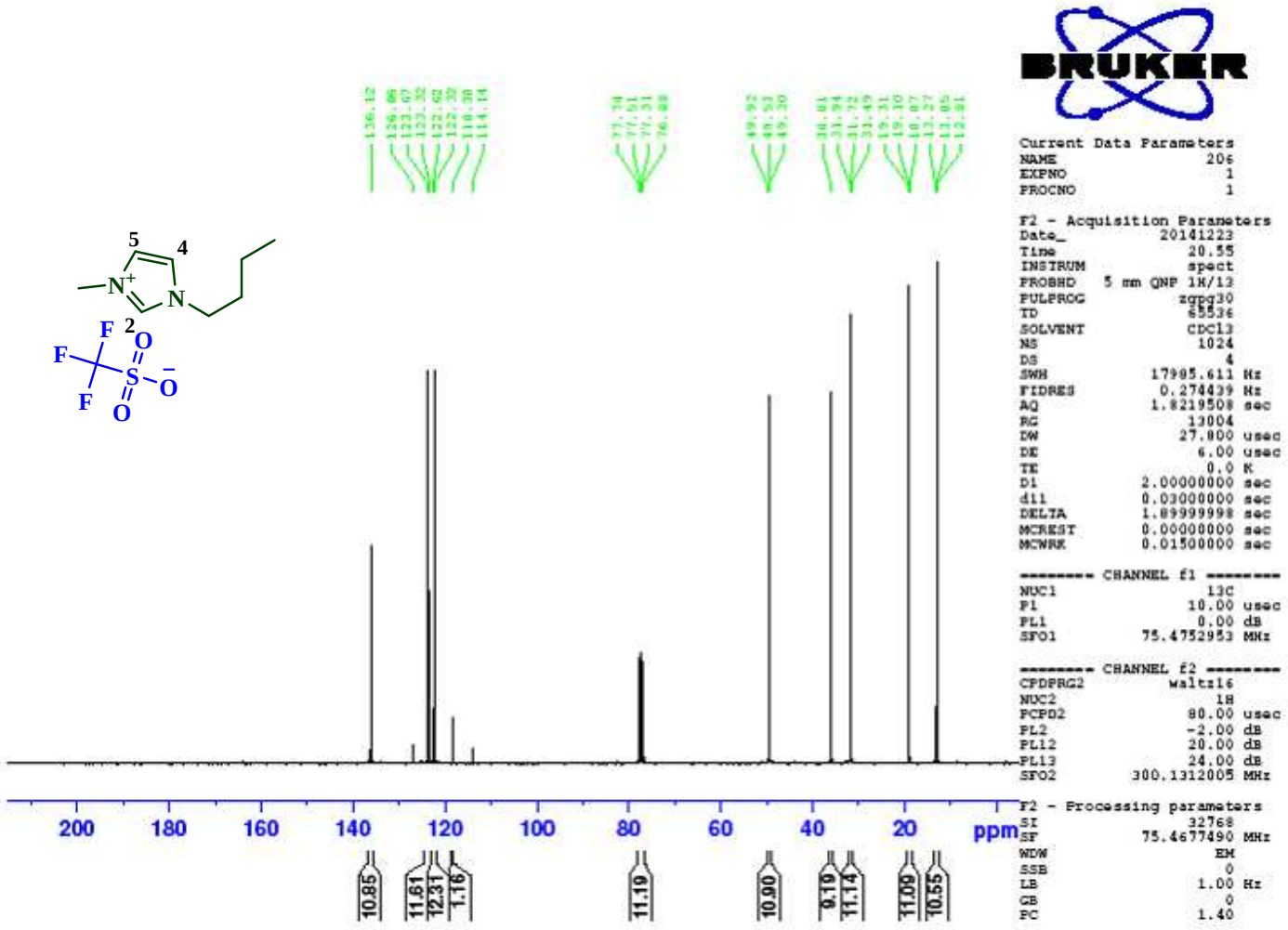

Fig. 2: ^{13}C NMR spectrum of **[Bmim]CF_3SO_3**

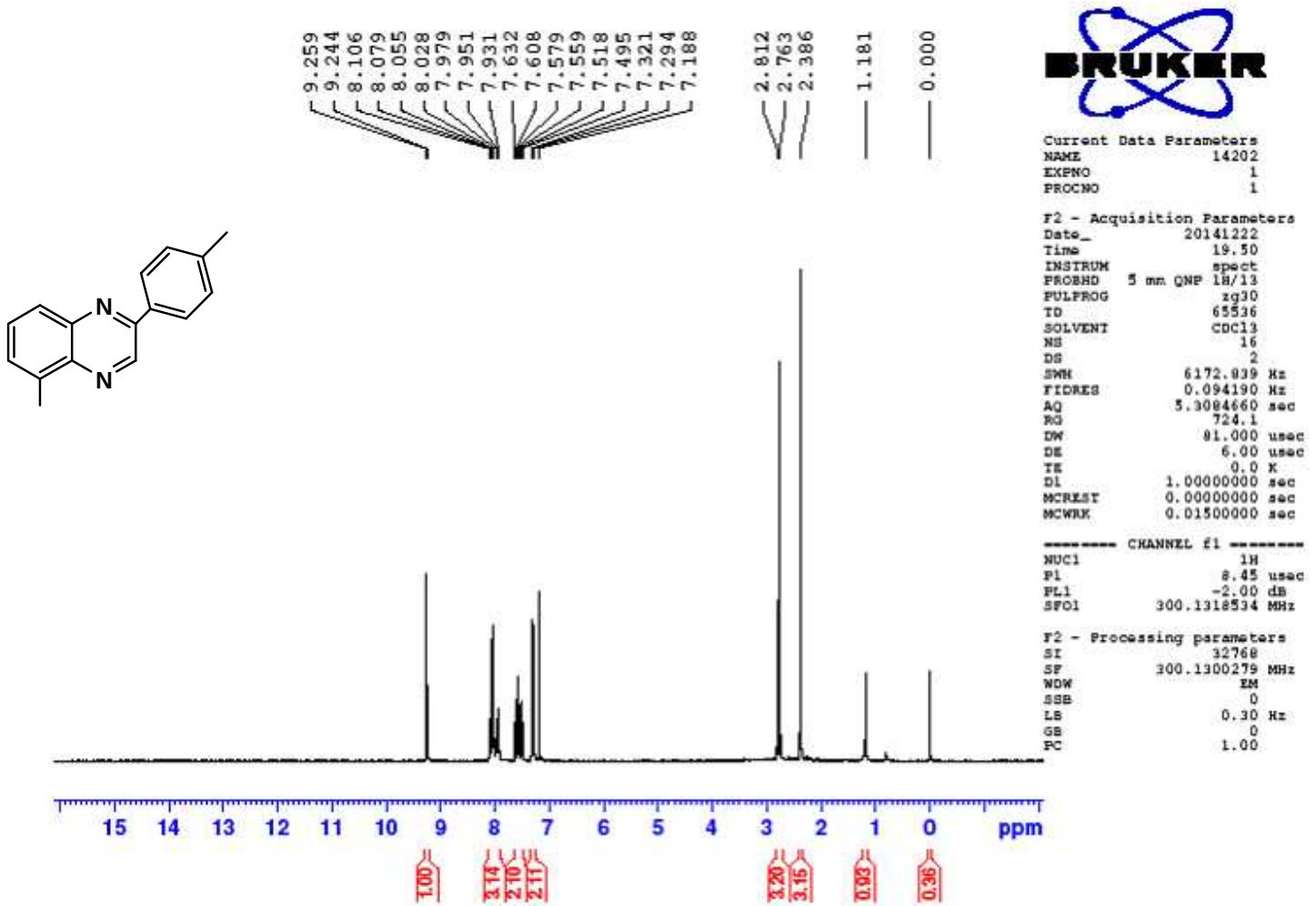

Fig. 3: ^{1}H NMR spectrum of **6g**

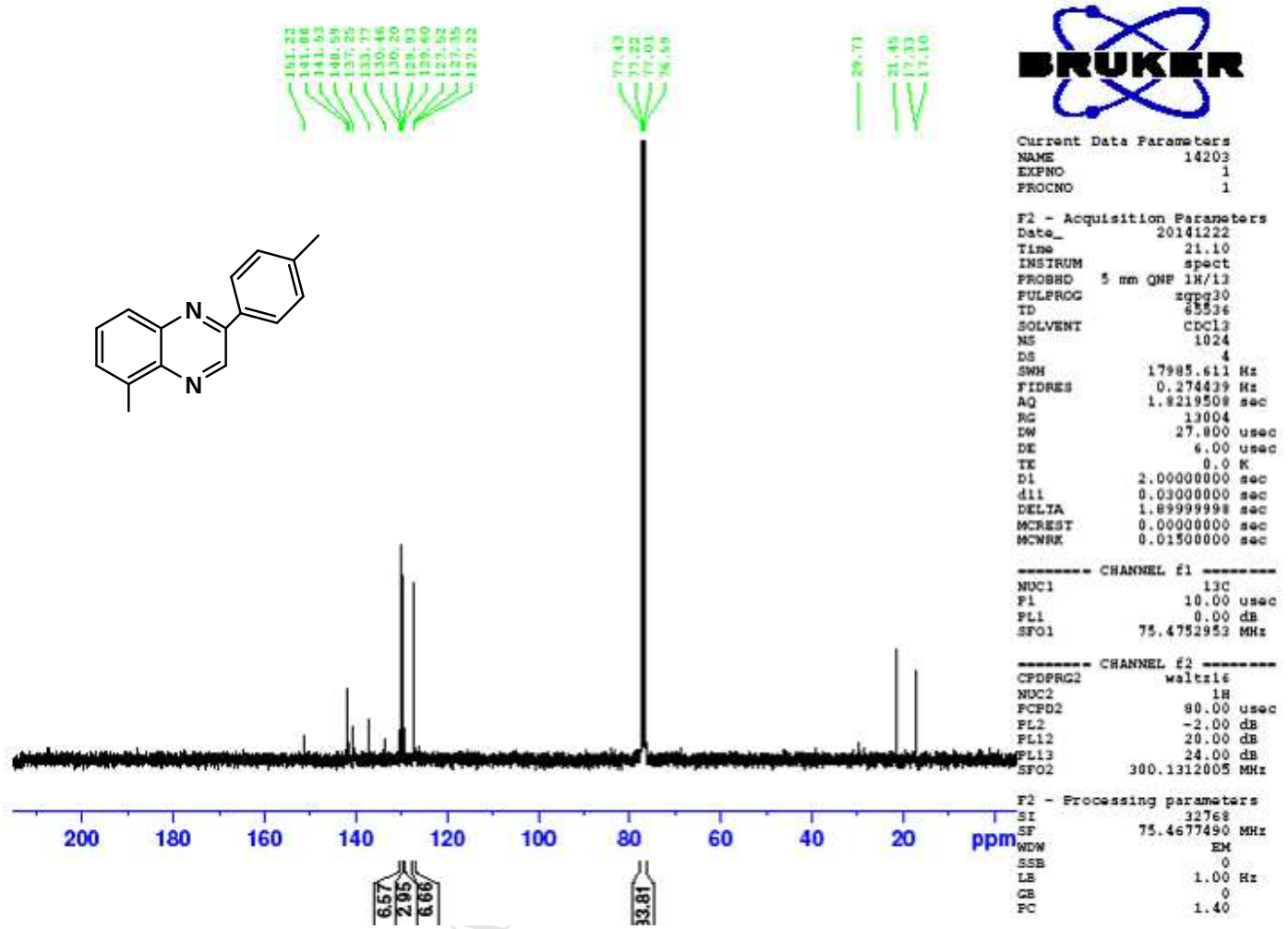

Fig. 4: ^{13}C NMR spectrum of **6g**

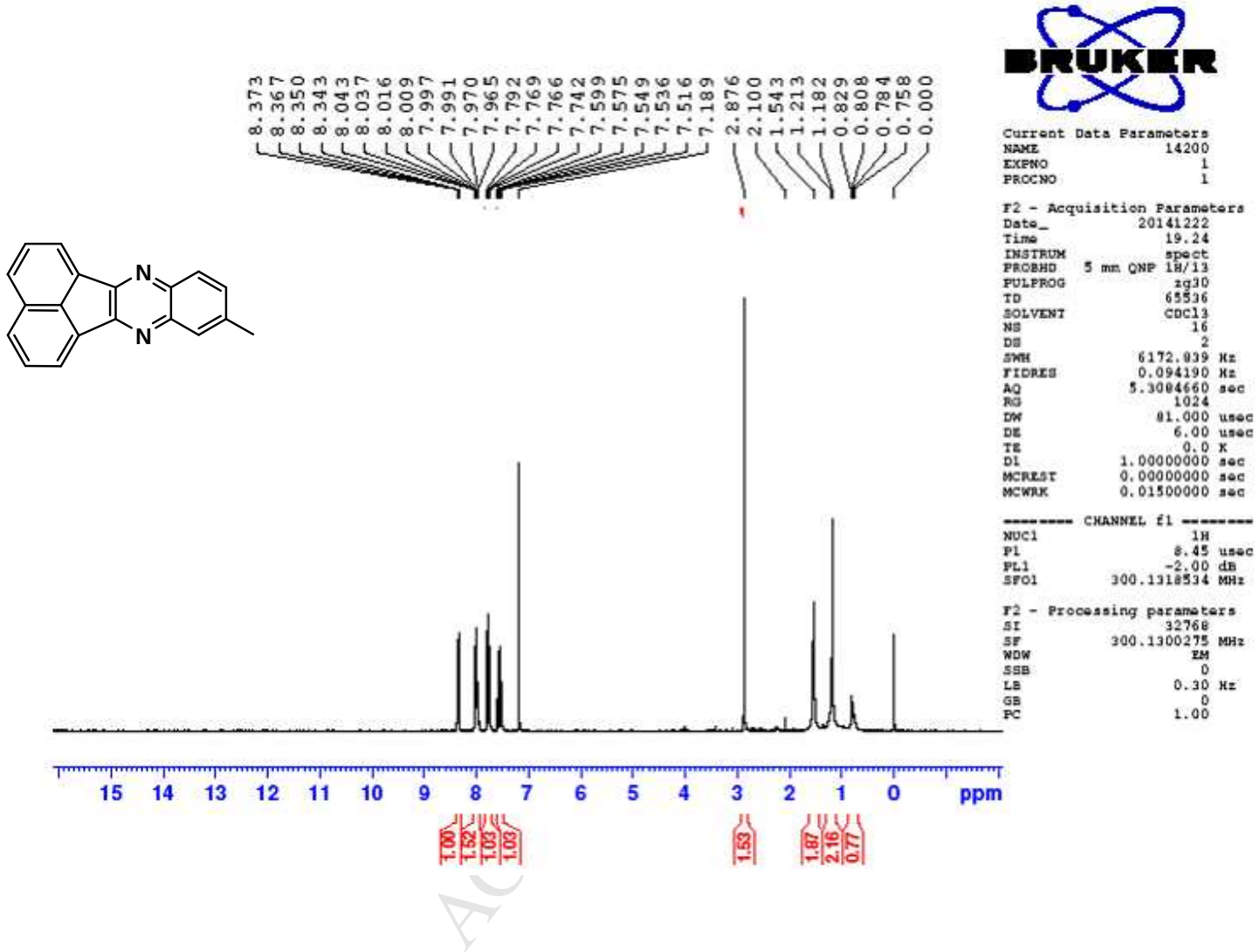

Fig. 5: ^{1}H NMR spectrum of **5b**

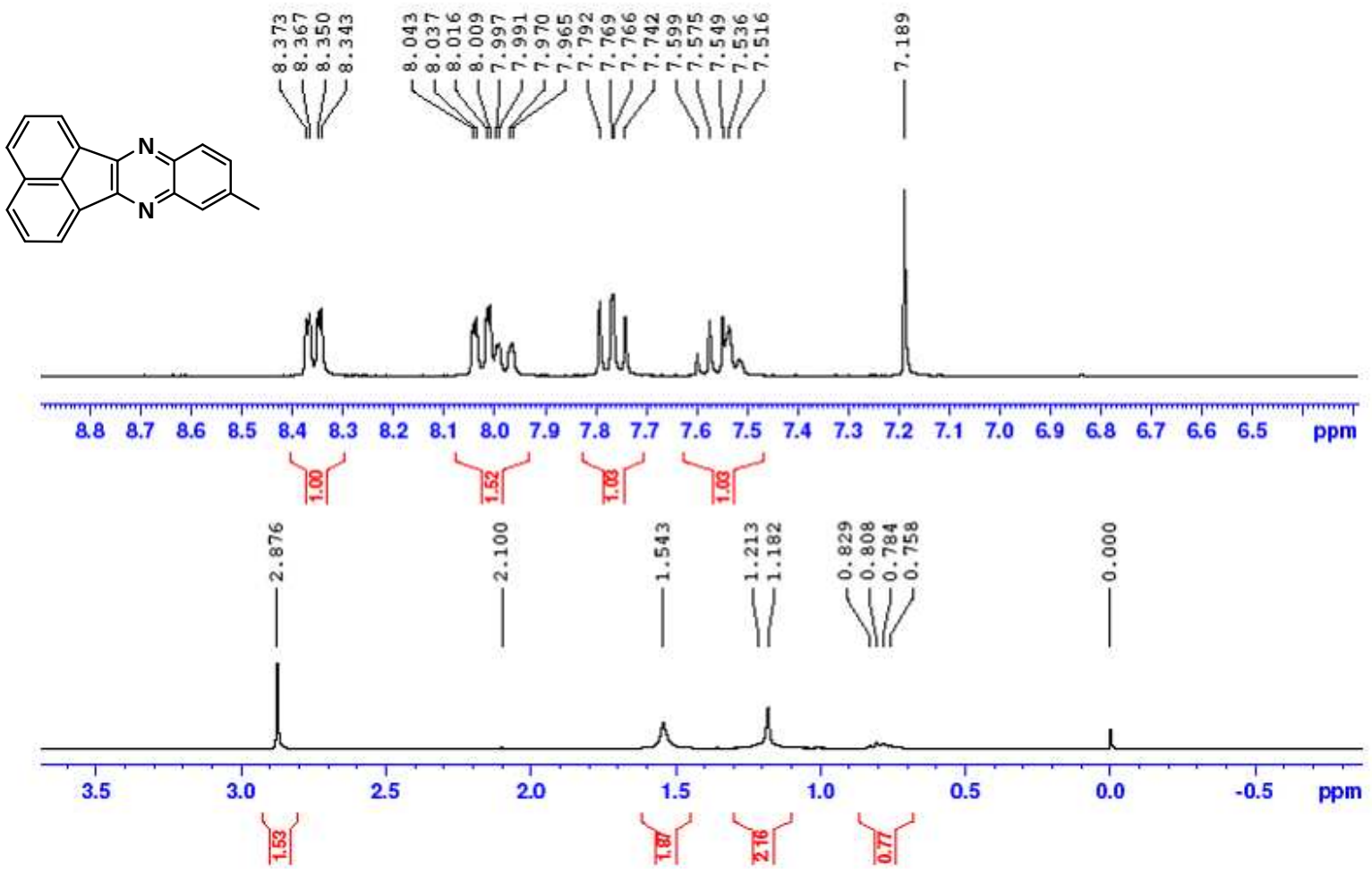

Fig. 6: Extended ^{1}H NMR spectrum of **5b**

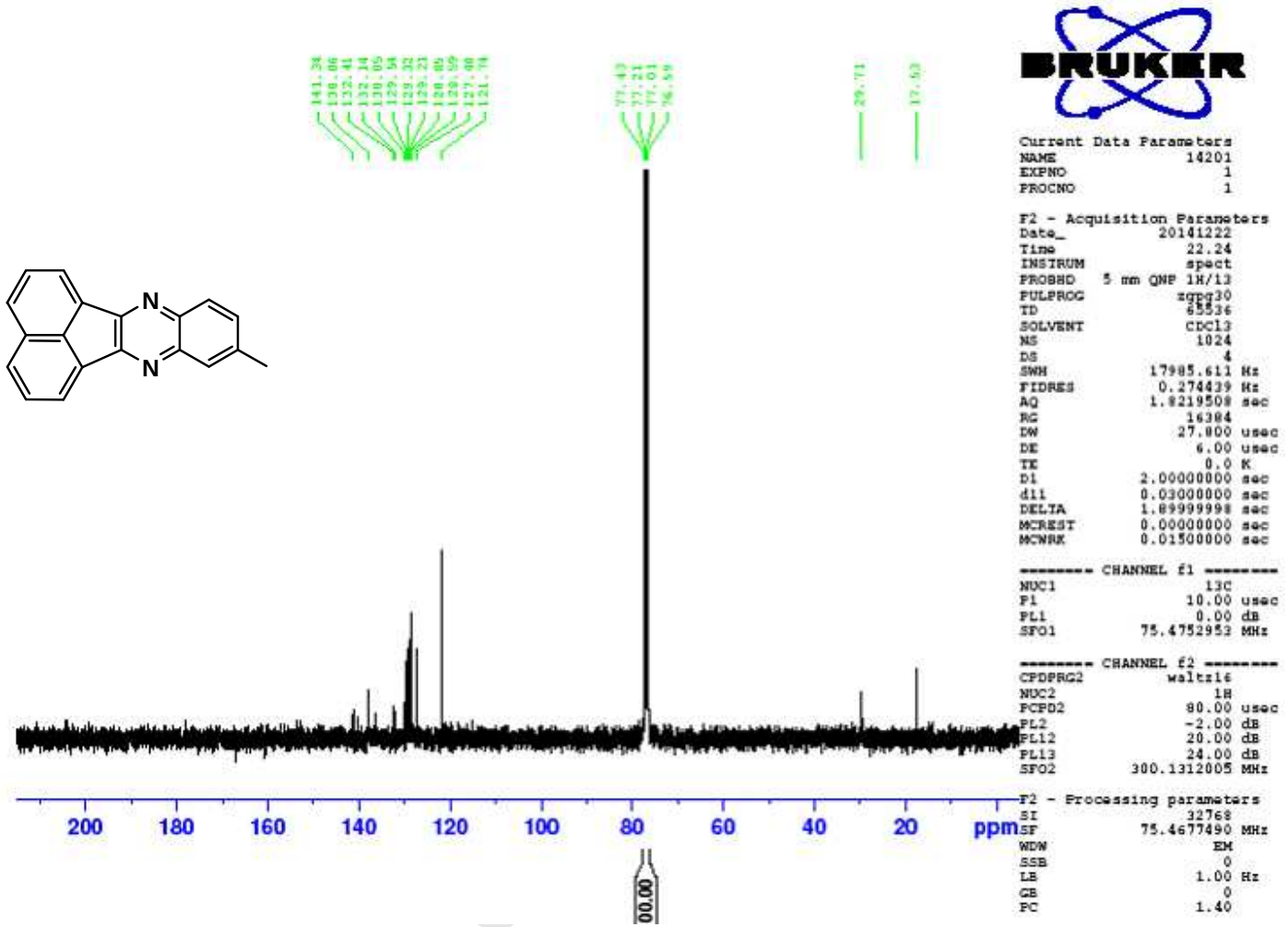

Fig. 7: ^{13}C NMR spectrum of **5b**

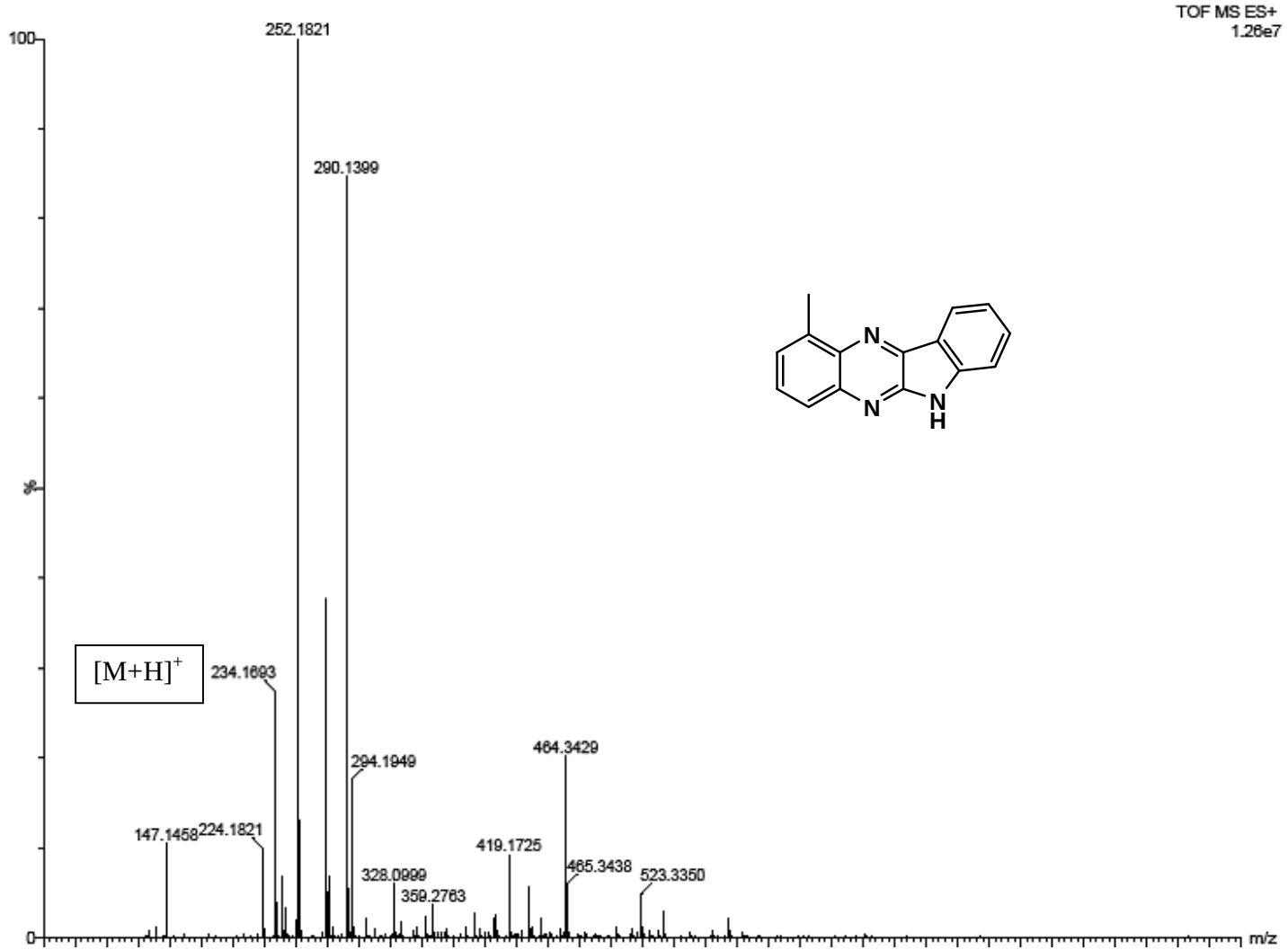

Fig. 8: MS spectrum of **4b**

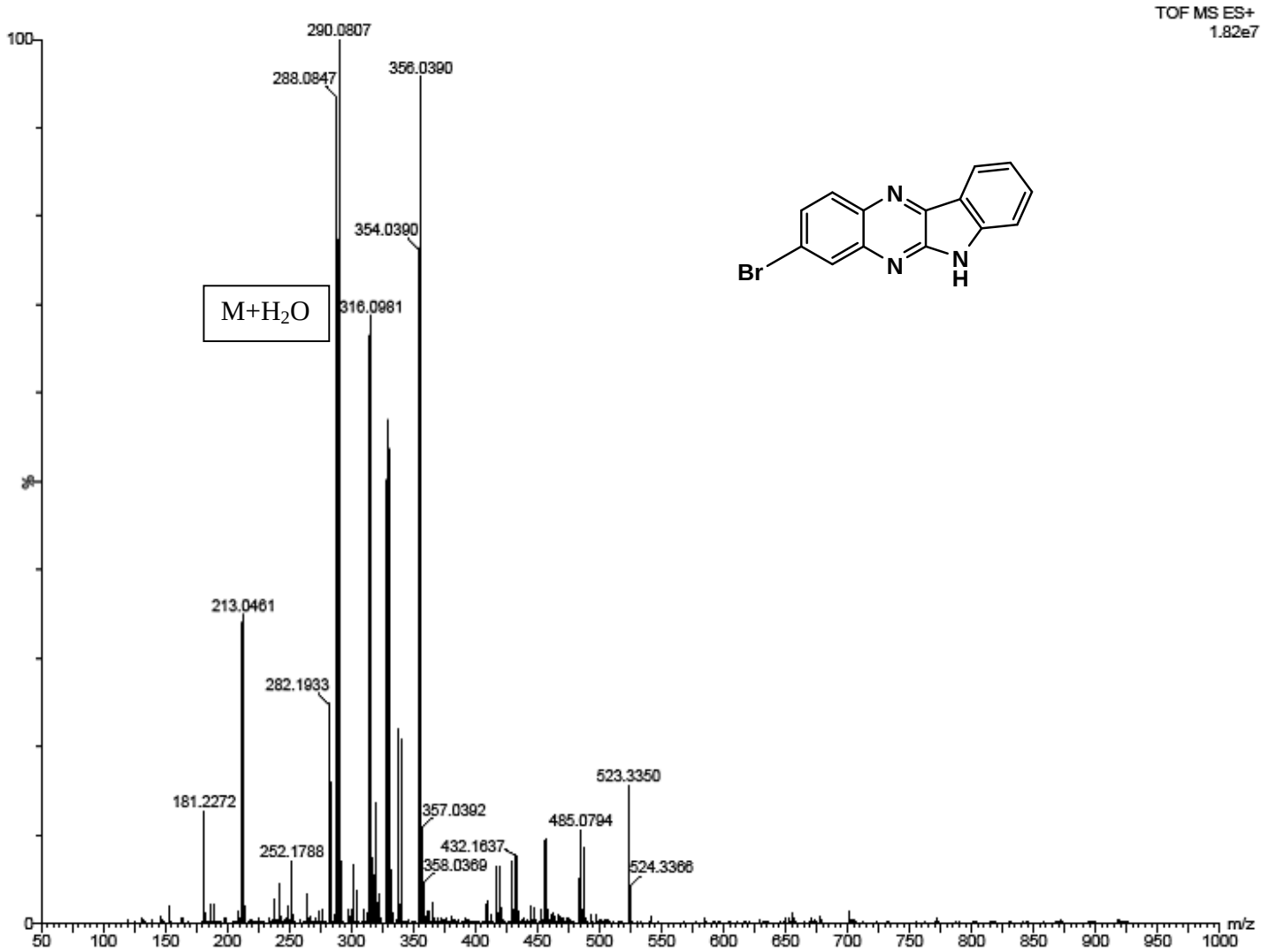

Fig. 9: MS spectrum of **4g**

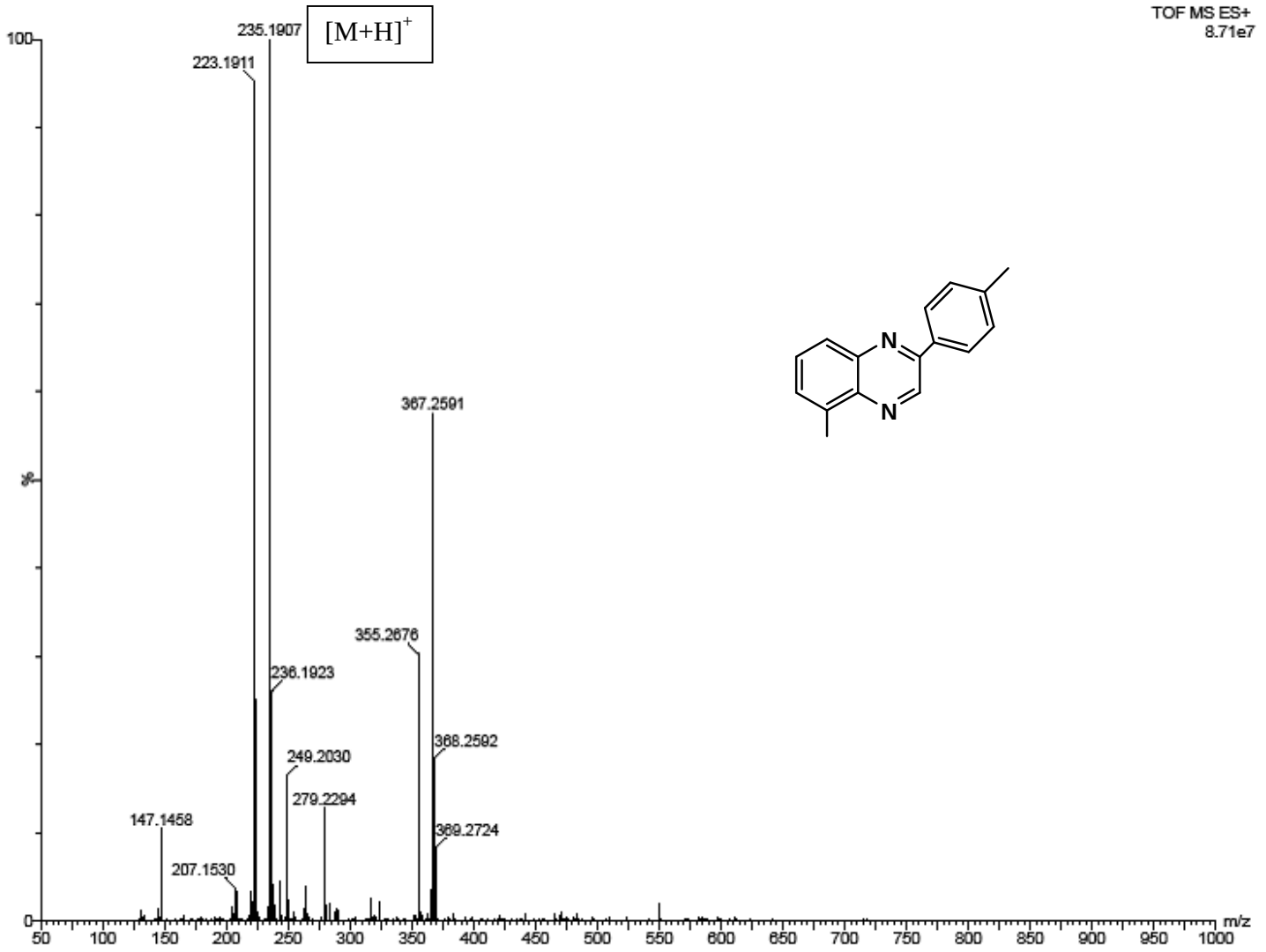

Fig. 10: MS spectrum of **6g**

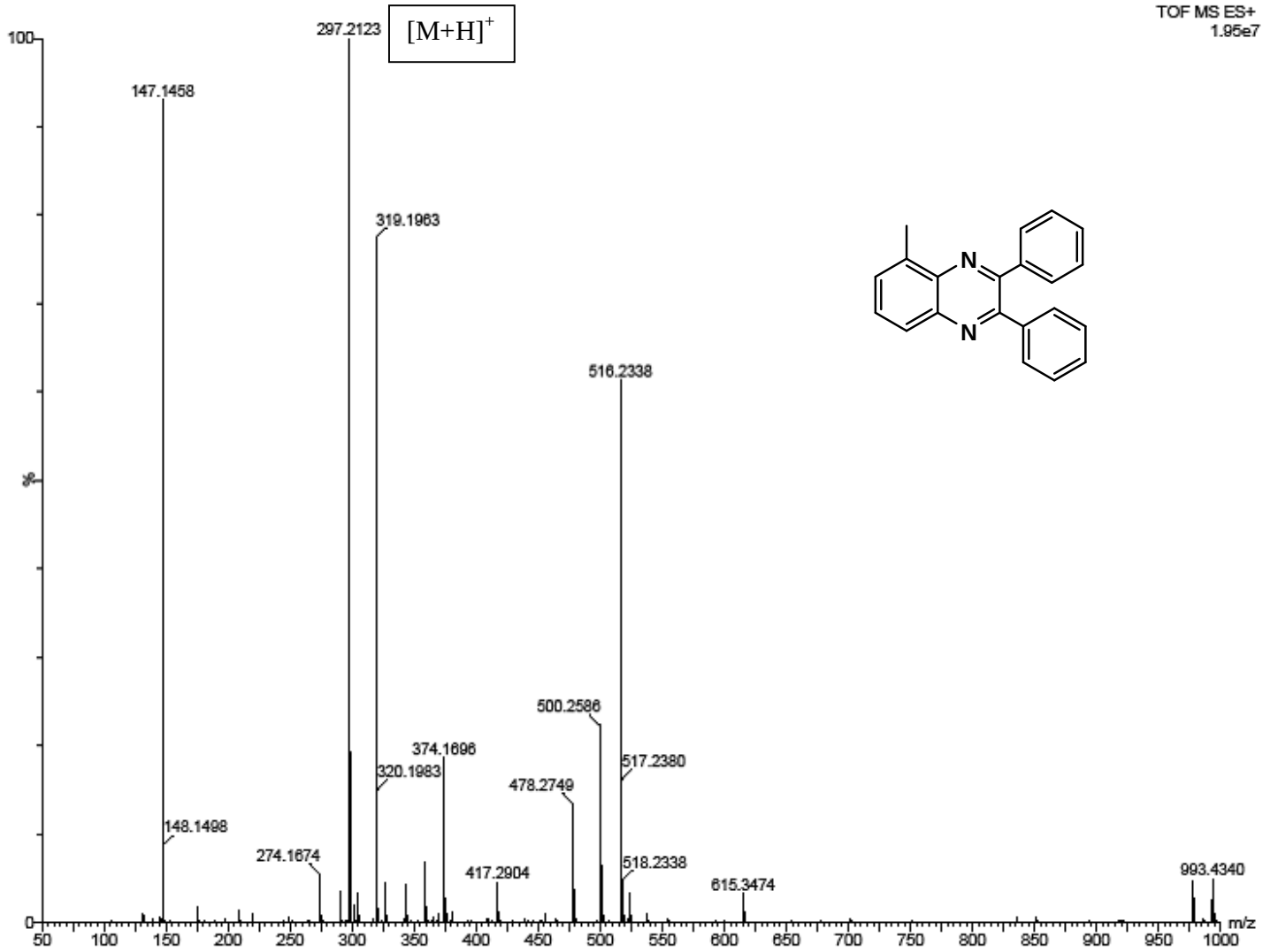

Fig. 11: MS spectrum of **3c**

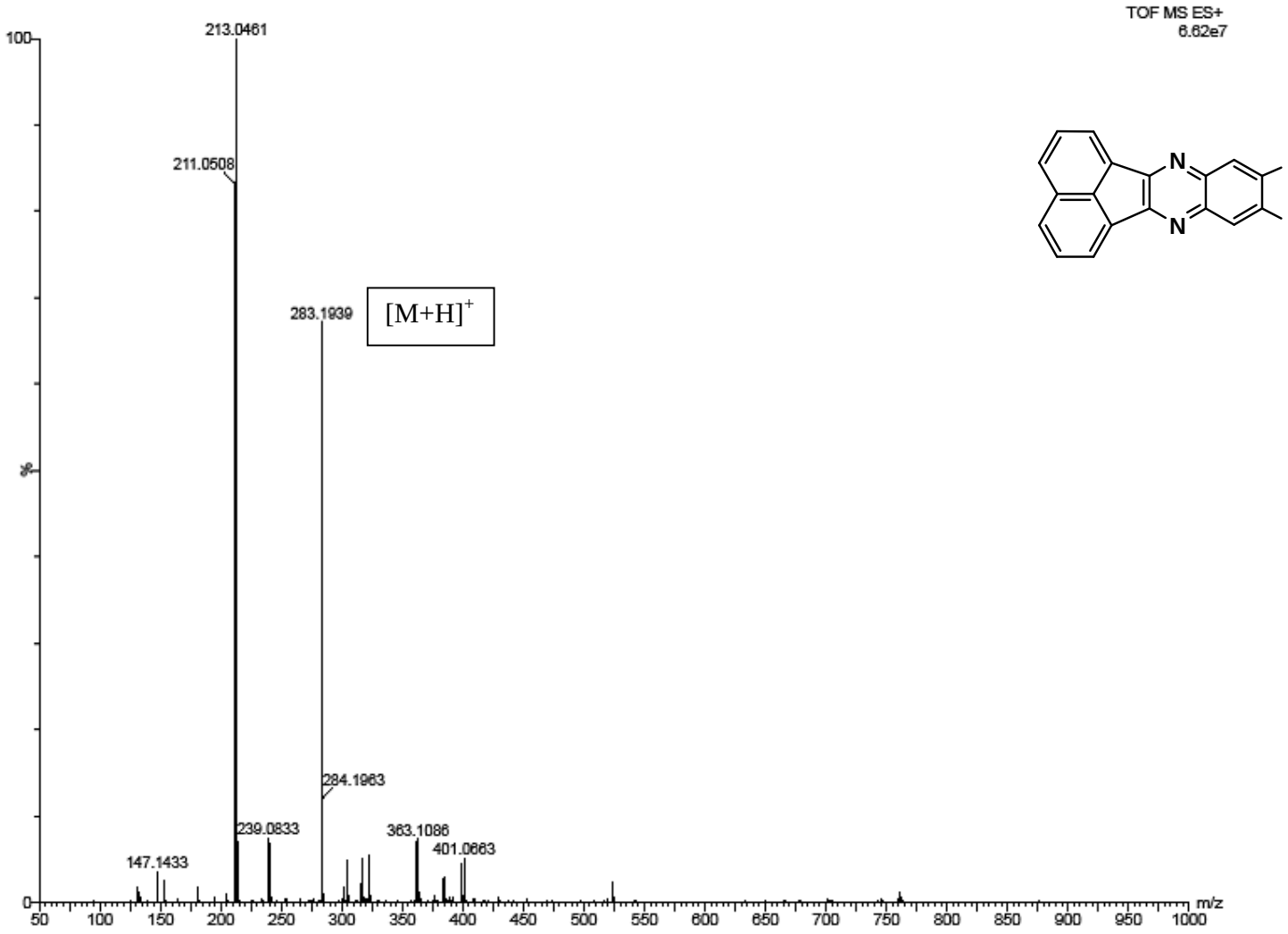

Fig. 12: MS spectrum of **5c**

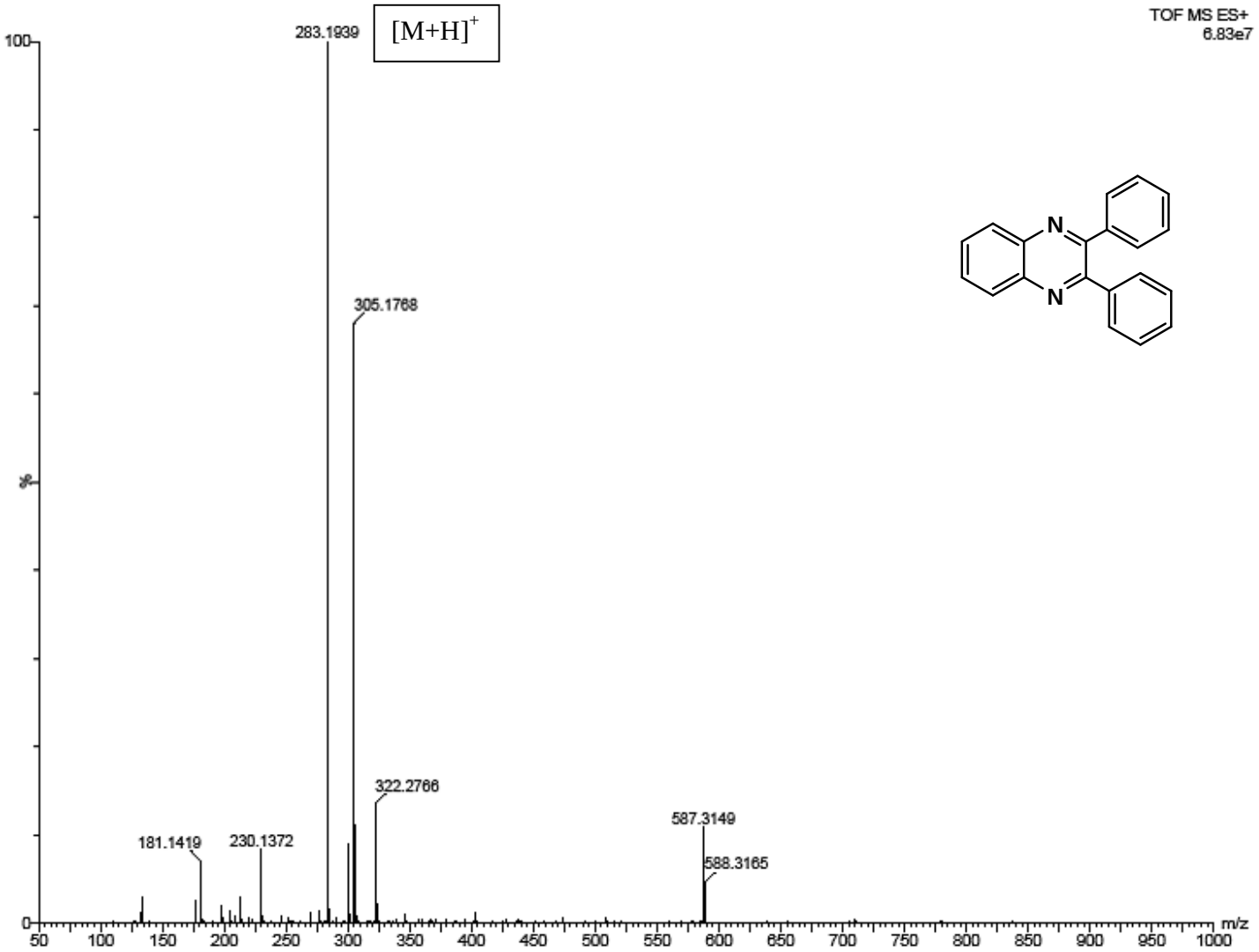

Fig. 13: MS spectrum of **3a**

An environmentally benign attribute for the expeditious synthesis of quinoxaline and its derivatives

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Research Highlights

- [Bmim]BF_4, [Bmim]CF_3SO_3, [Bmim]PF_6 are synthesized via simple procedure
- [Bmim]CF_3SO_3 is a most effective solvent and catalyst for the synthesis of quinoxalines
- Reusability of ionic liquid for six times
- No need of an additional catalyst
- Broad substrate applicability