JOC Article

Ionic Liquid-Promoted Regiospecific Friedlander Annulation: Novel Synthesis of Quinolines and Fused Polycyclic Quinolines

Sanjay S. Palimkar, Shapi A. Siddiqui, Thomas Daniel, Rajgopal. J. Lahoti, and Kumar V. Srinivasan*

Division of Organic Chemistry, Technology, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India

kvsri@dalton.ncl.res.in

Received August 6, 2003

Several room-temperature ionic liquids (ILs) based on 1-butylimidazolium salts with varying anions were synthesized and evaluated for the preparation of biologically active substituted quinolines and fused polycyclic quinolines using the Friedlander heteroannulation reaction. On screening, 1-butylimidazolium tetrafluoroborate [Hbim]BF_4 was found to be the best ionic liquid for the heteroannulation reaction, and the reasons to this effect are well explained. The reactions proceed very well under relatively mild conditions without any added catalyst. The IL acts as a promoter for this regiospecific synthesis and can be recycled. By this green approach, various quinolines were prepared in excellent yields and purity and well-characterized.

Introduction

The quinoline nucleus occurs in several natural compounds (cincona alkaloids) and pharmacologically active substances displaying a broad range of biological activity.[1] The biological activity of quinoline compounds has been found in the form of antiasthmatic,[2] antibacterial,[3] antiinflammatory[4] and antihypertensive[5] properties. In addition to the medicinal applications, quinolines have been employed in the study of bioorganic and bioorganometallic processes.[6] They are also known for their formation of conjugated molecules and polymers that combine enhanced electronic, optoelectronic, or nonlinear optical properties with excellent mechanical properties.[7]

The best-known method for quinolines and related polyheterocycles is the Friedlander quinoline synthesis.[8] Although it has been known for more than a century, it is still the most useful method for the preparation of such a class of compounds. Since 1882, the synthesis of the quinoline nucleus by the Friedlander procedure has been extensively explored.[9] Hydrochloric acid, sulfuric acid, *p*-toluenesulfonic acid and polyphosphoric acid were widely employed as catalysts.[10] In addition, microwave,[11] gold(III) compounds,[10] diphosgene/ acetonitrile solvent,[12]

* To whom correspondence should be addressed. Tel: +91-20-588 9089. Fax: +91-20-589 3614.

(1) (a) Chauhan, P. M. S.; Srivastava, S. K. *Curr. Med. Chem.* **2001**, *8*, 1535. (b) Balasubramanian, M.; Keay, J. G. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: New York, 1996; Vol. 5, p 245 (c) Yates, F. S. In *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., McKillop, A., Eds.; Pergamon Press: New York, 1984; Vol. 2, Chapter 2.09.

(2) (a) Larsen, R. D.; Corley, E. G.; King, A. O.; Carrol, J. D.; Davis, P.; Verhoeven, T. R.; Reider, P. J.; Labelle, M.; Gauthier, J. Y.; Xiang, Y. B.; Zamboni, R. J. *J. Org. Chem.* **1996**, *61*, 3398. (b) Zwaagstra, M. E.; Timmerman, H.; van de Stolpe, A. C.; de Kanter, F. J.; Tamura, M.; Wada, Y.; Zhang, M. Q. *J. Med. Chem.* **1998**, *41*, 1428. (c) von Sprecher, A.; Gerspacher, M.; Beck, A.; Kimmel, S.; Wiestner, H.; Anderson, G. P.; Niederhauser, U.; Subramanian, N.; Bray, M. A. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 965.

(3) (a) Mogilaiah, K.; Chowdary, D. S.; Rao, R. B. *Ind. J. Chem.* **2001**, *40B*, 43. (b) Chen, Y.-L.; Fang, K.-C.; Sheu, J.-Y.; Hsu, S.-L.; Tzeng, C.-C. *J. Med. Chem.* **2001**, *44*, 2374.

(4) (a) Roma, G.; Braccio, M. D.; Grossi, G.; Mattioli, F.; Ghia, M. *Eur. J. Med. Chem.* **2000**, *35*, 1021. (b) Kalluraya, B.; Sreenizasa, S. *Farmaco* **1998**, *53*, 399.

(5) (a) Morizawa, Y.; Okazoe, T.; Wang, S.-Z.; Sasaki, J.; Ebisu, H.; Nishikawa, M.; Shinyama, H. *J. Fluorine Chem.* **2001**, *109*, 83. (b) Ferrarini, P. L.; Mori, C.; Badawneh, M.; Calderone, V.; Greco, R.; Manera, C.; Martinelli, A.; Nieri, P.; Saccomanni, G. *Eur. J. Chem.* **2000**, *35*, 815.

(6) (a) Saito, I.; Sando, S.; Nakatani, K. *Bioorg. Med. Chem.* **2001**, *9*, 2381. (b) Nakatani, K.; Sando, S.; Saito, I. *J. Am. Chem. Soc.* **2000**, *122*, 2172. (c) Nguyen, C. H.; Marchand, C.; Delage, S.; Sun, J.-S.; Garestier, T.; Claude, H.; Bisagni, E. *J. Am. Chem. Soc.* **1998**, *120*, 2501.

(7) (a) Stille, J. K. *Macromolecules* **1981**, *14*, 870. (b) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806. (c) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 95. (d) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895. (e) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 633. (f) Jenekhe, S. A.; Lu. L.; Alam, M. M.; *Macromolecules* **2001**, *34*, 7315. (g) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837. (h) Jegou, G.; Jenekhe, S. A. *Macromolecules* **2001**, *34*, 7926. (i) Lu. L.; Jenekhe, S. A. *Macromolecules* **2001**, *34*, 6249. (j) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579. (k) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V. E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409. (k) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 7422. (l) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069.

(8) (a) Cheng, C.-C.; Yan, S.-J. In *Organic Reactions*; Dauben, W. G., Ed.; John Wiley & Sons: New York, 1982; Vol. 28, Chapter 2. (b) Friedlander, P. *Berichte* **1882**, *15*, 2572. For reviews of quinoline and naphthyridine syntheses, see: (c) Jones, G. In *Comprehensive Heterocyclic Chemistry II*; Ramsden, C. A., Ed.; Pergamon Press: Tarrytown, 1996; Vol. 5, Chapter 5.05. (d) Jones, G. In *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., McKillop, A., Eds.; Pergamon Press: New York, 1984; Vol. 2, Chapter 2.08. (e) Lowe, P. A. In *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., McKillop, A., Eds.; Pergamon Press: New York, 1984; Vol. 2, Chapter 2.11.

(9) Cheng, C.-C.; Yan, S.-J. In *Organic Reaction*; J. Wiley: New York, 1982; Vol. 28, p 37.

(10) Arcadi, A.; Chiarini, M.; Giuseppe, S. D.; Marinelli, F. *Synlett* **2003**, *2*, 203 and references therein.

(11) Song, S. J.; Cho, S. J.; Park, D. K.; Kwan, T. W.; Jenekhe, S. A. *Tetrahedron Lett.* **2003**, *44*, 255.

(12) Lee, B. S.; Lee, J. H.; Chi, D. Y. *J. Org. Chem.* **2002**, *67*, 7884.

10.1021/jo035153u CCC: $25.00
Published on Web 10/24/2003

$ZnCl_2$/triethylamine[13] and more recently a variety of amines[14] were also employed as promoters and catalysts. Many transition-metal-catalyzed Friedlander-type heteroannulation processes have been developed for the synthesis of quinolines. For example, several ruthenium, palladium, and iron complexes have been shown to catalyze the formation of 2,3-disubstiuted quinolines from nitrobenzene and aldehydes or alcohols in the presence of CO.[15] Also, aniline was shown to undergo N-heterocyclization to generate quinolines with aliphatic aldehydes with use of transition-metal complexes.[16] Uncatalyzed Friedlander synthesis required more drastic reaction conditions, with temperatures in the range 150−220 °C. Most of the synthetic protocols for quinolines reported so far suffer from harsh conditions, poor yields, prolonged time period, and use of hazardous and often expensive acid and base catalysts. Moreover, the synthesis of these heterocycles have been usually carried out in polar solvents such as acetonitrile, THF, DMF, and DMSO leading to complex isolation and recovery procedures. These processes also generate waste-containing solvent and catalyst, which have to be recovered, treated, and disposed of.

In recent years, studies of low waste routes and reusable reaction media for enhanced selectivity and energy minimization are the key interests of synthetic organic chemists world over.[17] In this context, in recent times, the use of room-temperature ionic liquids (ILs) as "green" solvents in organic synthetic processes has gained considerable importance due to their solvating ability, negligible vapor pressure, and easy recyclability.[18] They have the potential to be highly polar yet noncoordinating. In addition to the above-mentioned salient features of ILs as reaction media, we have also recently shown that they can also promote and catalyze organic transformations of commercial importance under ambient conditions without the need for any added catalyst or ligand. The reactions investigated by us are Heck and Suzuki reactions,[19] nitration of phenols,[20] and bromination of aromatics,[21] which proceed in significantly enhanced reaction rates, high regioselectivity and excellent isolated yields. In particular, we have recently reported the heterocyclization reaction of *o*-phenylenediamines with both acyclic and cyclic ketones in the IL 1,3-di-*n*- butylimidazolium bromide ([bbim]Br) to afford 1,5-benzodiazepines in excellent isolated yields in the absence of a catalyst at ambient temperature.[22]

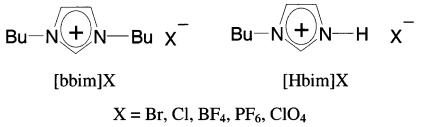
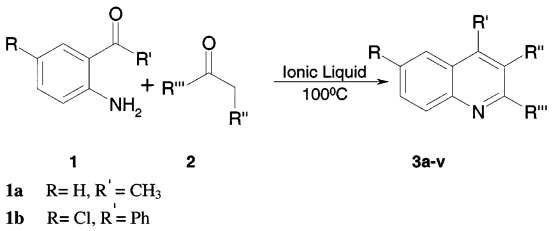


FIGURE 1. Ionic liquids synthesized, characterized, and screened.

SCHEME 1



Proceeding on the same lines, we chose to evolve an efficient and ecofriendly process for the preparation of quinolines and related polyheterocycles using the Friedlander heteroannulation protocol in the presence of the "green" imidazolium ionic liquids as reaction media as well as promoters in the absence of any added catalyst. Herein we disclose the successful outcome of this endeavor in which *o*-amino substituted aromatic carbonyls and ketones/diketones/ketoesters (containing active methylene groups) afforded excellent yields of the annulation products in the IL, 1-butylimidazolium tetrafluoroborate [Hbim]BF_4 among several ILs screened.

Results and Discussion

In view of the emerging importance of the imidazolium-based ILs as novel reaction media and as a part of our ongoing investigations of heterocyclization reactions based on such ILs, we wished to explore their use in the synthesis of the biologically important quinolines and related polyheterocycles using the Friedlander reaction conditions. For this purpose, 2-aminoacetophenone (**1a**) and 2-amino-5-chlorobenzophenone (**1b**) were reacted with a variety of ketones/ketoesters (**2**) in the ionic liquid as shown in Scheme 1.

Two sets of ILs based on *N*,*N*-di-*n*-butylimidazolium (bbim) and *N*-butylimidazolium (Hbim) salts with varying basicity of the anions were synthesized (Figure 1).

They were fully characterized by spectral and elemental analyses. For the [Hbim] ILs the chemical shifts for the NH protons were not observable in the ^{1}H NMR spectra when recorded in $CDCl_3$. However, the NH proton chemical shifts were observed as broad singlets with accompanying changes in the chemical shifts of the

(13) Jiang, B.; Si, Y, -G. *J. Org. Chem.* **2002**, *67*, 9449.
(14) Dormer, P. G.; Eng, K. K.; Farr, R. N.; Humphrey, G. R.; McWilliams, J. C.; Reider, P. J.; Sager, J. W.; Volante, R. P. *J. Org. Chem.* **2003**, *68*, 467.
(15) (a) Hegedus, L. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1113. (b) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667. (c) Watanabe, Y.; Suzuki, N.; Tsuji, Y.; Shim, S. C.; Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1116. (d) Watanabe, Y.; Tsuji, Y.; Shida, J. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 435. (e) Watanabe, Y.; Takatsuki, K.; Shim, S. C.; Mitsudo, T.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3397.
(16) (a)Watanabe, Y.; Tsuji, Y.; Ohsugi, Y.; Shida, J. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2452. (b) Watanabe, Y.; Shim, S. C.; Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3460. (c) Larock, R. C.; Hightower, T. R.; Hasvold, L. A.; Peterson, K. P. *J. Org. Chem.* **1996**, *61*, 3584. (d) Larock, R. C.; Kuo, M.-Y. *Tetrahedron Lett.* **1991**, *32*, 569. (e) Beller, M.; Thiel, O. R.; Trauthwein, H.; Hartung, C. G. *Chem. Eur. J.* **2000**, *6*, 2513.
(17) (a) Horvath, I. T.; Rabai, J. *Science* **1994**, *266*, 72. (b) Chauvin, Y., Olivier-Bourbigou, H. *CHEMTECH* **1995**, *25*, 26. (c) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351. (d) Kitazume, T.; Ishizuka, T.; Takedu, M.; Itoh, K. *Green Chem.* **1999**, *1*, 221.
(18) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Wasserscheid P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. (c) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391. (d) Gordon, C. M. *Appl. Catal. A: General* **2001**, *222*, 101. (e) Sheldon, R. *Chem. Commun.* **2001**, 2399.
(19) (a) Deshmukh, R. R.; Rajagopal, R.; Srinivasan, K. V. *Chem. Commun.* **2001**, 1544. (b) Rajagopal, R.; Jarikote, D. V.; Srinivasan, K. V. *Chem. Commun.* **2002**, 616.
(20) (a) Rajagopal, R.; Srinivasan, K. V. *Synth. Commun.* **2003**, *33*, 961. (b) Rajagopal, R.; Srinivasan, K. V. *Ultrson. Sonochem.* **2003**, *10*, 45.
(21) Rajagopal, R.; Jarikote, D. V.; Thomas Daniel; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron Lett.* **2003**, *44*, 1815.
(22) Jarikote, D. V.; Siddiqui, S. A.; Rajagopal, R.; Thomas Daniel; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron Lett.* **2003**, *44*, 1835.

TABLE 1. Synthesis of 3c in [bbim] ILs

IL	pK_a of acid of the anion, HX	yield[a] (%)
[bbim]ClO_4	−11	37
[bbim]Br	−9	50
[bbim]Cl	−7	50
[bbim]PF_6		70
[bbim]BF_4	0.5	75

[a] Isolated yield after column chromatography.

TABLE 2. Synthesis of 3c in [Hbim] ILs

IL	pK_a of acid of the anion, HX	chemical shift −NH proton δ (ppm)	yield[a] (%)
[Hbim]ClO_4	−11	11.83	50
[Hbim]Br	−9	12.17	75
[Hbim]Cl	−7	12.22	73.8
[Hbim]PF_6		12.61	90
[Hbim]BF_4	0.5	14.59	96

[a] Isolated yield after column chromatography.

imidazolium protons of the ILs when the ^{1}H NMR spectra were recorded neat using $CDCl_3$ as external lock. In mass spectra, all the ILs showed [M − X] as the base peak and peaks corresponding to the molecular ion were not observed. The elemental analyses of the ILs were in conformity with their structures.

The synthesized new ILs were then tested as solvents and promoters for the typical reaction of *o*-amino acetophenone (**1a**) with cyclopentanone in the absence of any added catalyst to afford 9-methyl-2, 3-dihydro-1*H*-cyclopenta[*b*]quinoline (**3c**). The reactions in the various ILs were carried out at 100 °C for 24 h. The yield data are recorded in Tables 1 and 2.

The efficacy of the ILs to promote these heterocyclization reactions was correlated to the basicity of the anions of the ILs. It was 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. Thus, the yield of 9-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**3c**) for the reaction in different ILs was compared against the pK_a values of the corresponding acid of the anion (Tables 1 and 2). The pK_a values were obtained from literature.[23] It was observed that with increasing basicity of the anion (increasing pK_a of the corresponding acid) there is a progressive increase in yield.

This correlation was more evident in the case of [Hbim] ILs when the yield of **3c** was compared with −NH proton chemical shifts of the ILs indicative of the Bronsted acidities of the ILs (Table 2). The yield of **3c** increases progressively with increasing Bronsted acidity of the ILs as indicated by the increasing downfield shift of the NH proton**.**

It becomes evident from the foregoing results, the IL [Hbim]BF_4 afforded the best results. Consequently, all further studies were conducted using this IL as the reaction medium. The reaction of *o*-aminoacetophenone (**1a**) with cyclopentanone (**2**) in [Hbim]BF_4 was then carried out at temperatures below and above 100 °C, respectively. At 90 °C, the conversion does not go beyond 30% even after 24 h. At 130 °C, the reflux temperature of cyclopentanone, the IL decomposed to give a black charry material. This was further confirmed by running a thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG) analysis and differential thermal analysis (DTA) of a pure sample of [Hbim]BF_4. The thermal decomposition started at 152.7 °C, and at 335.3 °C complete weight loss was observed. An endotherm which was observed at 324.5 °C in DTA may be the result of the decomposition of the BF_4 species into the stable BF_3 and F^-. Hence, all subsequent reactions using this IL were carried out at 100 °C.

The IL [Hbim]BF_4 was used as a reaction medium and promoter to generate a variety of quinolines and fused polycyclic quinolines (**3a**−**v**) by the reaction of 2-aminoacetophenone (**1a**) and 2-amino-5-chlorobenzophenone (**1b**) with cyclic/acyclic ketones and keto esters (**2**), respectively. The results are recorded in Table 3. All the reactions proceed to completion at the time indicated in the Table 3 without any catalyst, and the yield data are for the isolated products. All the compounds were well characterized by melting point, IR, ^{1}H NMR, ^{13}C NMR, and mass spectral analyses. Their elemental analyses were in conformity with their structures. In all the cases, the IL could be recovered almost completely (98%) and recycled twice with only a very marginal loss in yield (1−2%) in the second recycle. The respective quinolines and polyheterocycles (**3a**−**v**) were obtained in high regioselectivity and could be isolated in excellent yields in all cases.

Theoretically, the Friedlander reaction with unsymmetrical ketones such as ethyl methyl ketone can have two possible modes of cyclization giving rise to two regioisomers viz., 2,3-dimethylquinoline and 2-ethylquinoline, respectively. Depending upon the catalyst, the modes of cyclization can change. In the Bronsted acid catalyzed reaction, 2,3-dimethylquinoline was reported to be the major product (80%) along with minor amounts (20%) of the 2-ethylquinoline, whereas under basic conditions, the 2-ethylquinoline was the major product and 2,3-dimethylquinoline was the minor product.[24] To our surprise, however, the ionic liquid promoted Friedlander reaction with unsymmetrical ketones such as ethyl methyl ketone/benzyl acetone respectively afforded regiospecifically the 2,3-dialkylquinoline only in excellent isolated yields (entries 7, 8, 18, and 19). No trace of the isomeric 2-ethylquinoline could be detected either on TLC or in ^{1}H NMR of the crude product mixture before purification by column chromatography. The relatively mild conditions of the reaction and the absence of Bronsted/Lewis acid catalyst, both factors promoted by the use of the IL as the reaction medium may have contributed to this phenomenon. Additionally, the polarity and the large electrochemical window of the IL may also have contributed to the observed regiospecificity.

Conclusion

It is clear from our results that the ionic liquid catalyzed reaction of *o*-amino substituted aromatic carbonyls with cyclic and acyclic ketones provides an efficient new tool for the regiospecific synthesis of quino-

(23) (a) Perrin, D. D. *Ionization Constant of Inorganic acids and bases in aqueous solution*, 2nd ed.; Pergamon: Elmsford, NY, 1982. (b) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973.

(24) Fennel, E. A. *J. Heterocycl. Chem.* **1966**, *31*, 2899.

TABLE 3. Synthesis of the Quinolines 3a–v in [Hbim]BF_4

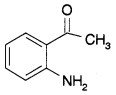
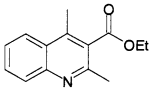
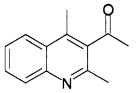
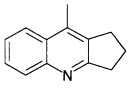
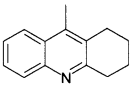
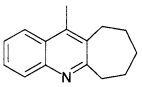
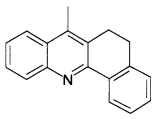
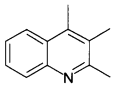
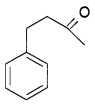
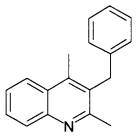
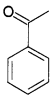
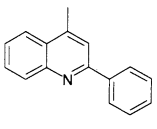
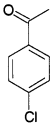
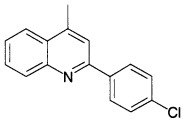
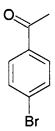
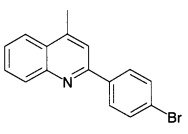
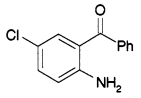
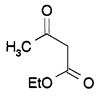
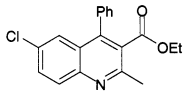
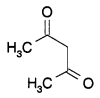
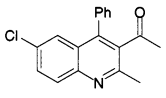
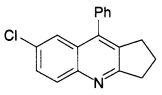
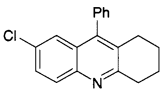
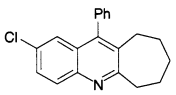
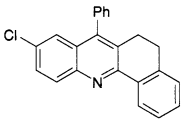
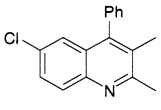
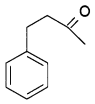
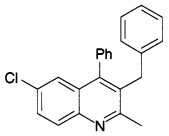
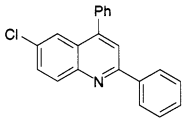
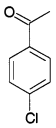
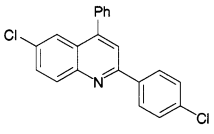
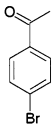
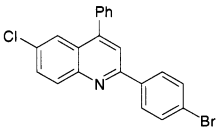
Entry	Compound 1	Compound 2	Product 3a-v	Time (h)	Yield [a] (%) First	Recycle I	Recycle II
1	 **1a**		 **3a**	3	94	93	93
2	**1a**		 **3b**	3.3	94	94	93
3	**1a**		 **3c**	3	96	95	94
4	**1a**		 **3d**	3	96	96	94
5	**1a**		 **3e**	3	97	96	95
6	**1a**		 **3f**	4	94	94	93
7	**1a**		 **3g**	6	93	92	90
8	**1a**		 **3h**	3.3	93	93	91
9	**1a**		 **3i**	6	93	92	91
10	**1a**		 **3j**	6	94	93	92
11	**1a**		 **3k**	6	94	94	93

Table 3 (Continued)

Entry	Compound 1	Compound 2	Product 3a-v	Time (h)	Yield [a] (%) First	Recycle I	Recycle II
12	 **1b**		 **3l**	3	94	94	93
13	**1b**		 **3m**	3.3	93	93	91
14	**1b**		 **3n**	3	97	96	95
15	**1b**		 **3o**	3	98	96	96
16	**1b**		 **3p**	3	97	95	95
17	**1b**		 **3q**	4	93	92	91
18	**1b**		 **3r**	6	91	90	90
19	**1b**		 **3s**	3.3	93	93	92
20	**1b**		 **3t**	6	92	92	90
21	**1b**		 **3u**	6	90	90	88
22	**1b**		 **3v**	6	92	92	90

[a] Isolated yield.

lines and fused polycyclic quinolines under relatively mild conditions. In conclusion, we have developed a green approach to Friedlander synthesis of quinolines that requires neither harsh conditions nor the use of hazardous acids or bases. The solvent IL can be recovered and reused twice without any loss of activity. Several new ILs were synthesized, characterized and screened for this heterocyclization reaction. The efficacy of the ILs for the heterocyclization reaction has been correlated to the acidity of the ILs in terms of basicity of the anions and ^{1}H NMR chemical shifts. The moderate reaction conditions, absence of a catalyst and recyclability of the nonvolatile IL makes this an environment friendly methodology amenable for scale-up.

Experimental Section

General Considerations. For Hbim IL series, ^{1}H NMR was taken neat using $CDCl_3$ as an external lock and for bbim series solutions in $CDCl_3$ were used for the spectra. Melting points were taken in open capillary and are uncorrected. Column chromatography was performed using silica gel (60−120 mesh size), and TLC was carried out using aluminum sheets precoated with silica gel $60F_{254}$. All solvents and chemicals used were reagent grade procured commercially and used without further purification.

Preparation of Different Ionic Liquids. 1,3-Di-*n*-butylimidazolium Bromide [bbim]Br. A mixture of 1-*n*-butylimidazole (12.4 g, 0.1 mol) and *n*-butyl bromide (15.0 g, 0.11 mol) was heated with stirring at 70 °C for 4 h. Excess *n*-butyl bromide was distilled off at 80 °C under reduced pressure (10 mm Hg) over 2 h leaving behind the product [bbim]Br: colorless liquid (25.06 g; yield 96%); IR (KBr) ν = 3401, 3067, 2874, 1635, 1563, 1465, 1167, 753 cm^{-1}; ^{1}H NMR δ = 0.74 (t, J = 7.0 Hz, 6H, CH_3), 1.13 (sept, J = 7.6 Hz, 4H, $CH_3CH_2(CH_2)_2N$), 1.69 (pent, J = 7.5 Hz, 4H, NCH_2CH_2), 4.13 (t, J = 7.0 Hz, 4H, NCH_2), 7.47 (s, 2H, NC*H*C*H*N), 10.08 (s, 1H, NC*H*N); ^{13}C NMR δ = 12.4, 18.4, 31.1, 48.7, 121.6, 135.6; MS *m*/*z* 181 (M − X, 31), 165 (3), 151 (6), 138 (37), 124 (53), 109 (8), 97 (100), 81 (87), 68 (21), 57 (29). Anal. Calcd for $C_{11}H_{21}N_2Br$ (261): C, 50.57; H, 8.05; N, 10.73. Found: C, 50.24; H, 7.91; N, 10.54.

1,3-Di-*n*-butylimidazolium Chloride [bbim]Cl. A mixture of 1-*n*-butylimidazole (12.4 g, 0.1 mol) and *n*-butyl chloride (10.17 g, 0.11 mol) was refluxed in toluene for 8 h. Toluene and excess *n*-butyl chloride were distilled off at 80 °C under reduced pressure (10 mm Hg) over 2 h leaving behind the product [bbim]Cl: viscous oil (20.61 g; yield 95%); IR (KBr) ν = 3401, 3067, 2874, 1635, 1563, 1465, 1167, 753 cm^{-1}; ^{1}H NMR δ = 0.80 (t, J = 7.0 Hz, 6H, CH_3), 1.24 (sept, J = 7.6 Hz, 4H, $CH_3CH_2(CH_2)_2N$), 1.72 (pent, J = 7.5 Hz, 4H, NCH_2CH_2), 4.22 (t, J = 7.0 Hz, 4H, NCH_2), 7.48 (s, 2H, NC*H*C*H*N), 10.38 (s, 1H, NC*H*N); ^{13}C NMR δ = 13.1, 19.1, 31.9, 49.3, 122.2, 136.9; MS *m*/*z* 181 (M − X, 31), 165 (3), 151 (6), 138 (37), 124 (53), 109 (8), 97 (100), 81 (87), 68 (21), 57 (29). Anal. Calcd for $C_{11}H_{21}N_2Cl$ (217): C, 60.82; H, 9.67; N, 12.9. Found: C, 60.64; H, 9.71; N, 12.81.

1,3-Di-*n*-butylimidazolium Tetrafluoroborate [bbim]BF_4. To a solution of 1,3-di-*n*-butylimidazolium bromide ([bbim]Br) (10 g, 0.1 mol) in water (50 mL) was added a solution of sodium tetrafluoroborate (5.11 g, 1.2 mol) in water (25 mL), and the mixture was stirred at 30 °C for 5 h. The ionic liquid [bbim]BF_4 separated out as an immiscible layer. The mixture was extracted with dichloromethane (3 × 30 mL). The combined DCM (dichloromethane) layer, which was separated, was washed with water and brine and dried over anhydrous sodium sulfate. The solvent DCM was distilled off under reduced pressure leaving behind the pure IL [bbim]BF_4: viscous oil (8.72 g; yield 86%); IR (KBr) ν = 3401, 3067, 2874, 1635, 1563, 1465, 1167, 753 cm^{-1}; ^{1}H NMR δ = 0.96 (t, J = 7.0 Hz, 6H, CH_3), 1.40 (sept, J = 7.6 Hz, 4H, $CH_3CH_2(CH_2)_2N$), 1.97 (pent, J = 7.5 Hz, 4H, NCH_2CH_2), 4.41 (t, J = 7.0 Hz, 4H, NCH_2), 7.87 (s, 2H, NC*H*C*H*N), 9.20 (s, 1H, NC*H*N); ^{13}C NMR δ = 12.9, 18.9, 31.6, 49.3, 122.2, 135.2; MS *m*/*z* 181 (M − X, 100), 165 (15), 151 (12), 138 (61), 124 (40), 107 (33), 97 (65), 81 (62), 68 (16), 57 (42). Anal. Calcd for $C_{11}H_{21}N_2BF_4$ (268): C, 49.25; H, 7.83; N, 10.44. Found: C, 49; H, 7.71; N, 10.21.

Similarly, other ionic liquids such as [bbim]PF_6 and [bbim]ClO_4 were prepared as above using the corresponding acid of the anion.

1,3-Di-*n*-butylimidazolium hexafluorphosphate [bbim]PF_6: viscous oil (11.17 g; yield 92%); IR (KBr) ν = 3603, 3146, 2936, 1565, 1466, 1166, 1091, 754, 623 cm^{-1}; ^{1}H NMR δ = 0.89−0.92 (t, J = 7.0 Hz, 6H, CH_3), 1.29−1.34 (sept, J = 7.6 Hz, 4H, $CH_3CH_2(CH_2)_2N$), 1.81−1.84 (pent, J = 7.5 Hz, 4H, NCH_2CH_2), 4.15−4.18 (t, J = 7.0 Hz, 4H, NCH_2), 7.35 (s, 2H, NC*H*C*H*N), 8.86 (s, 1H, NC*H*N); ^{13}C NMR δ = 13.1, 19.2, 31.8, 49.8, 122.4, 135.2; MS *m*/*z* 181 (M − X, 100), 165 (15), 151 (12), 138 (61), 124 (40), 107 (33), 97 (65), 81 (62), 68 (16), 57 (42). Anal. Calcd for $C_{11}H_{21}N_2PF_6$ (325): C, 40.61; H, 6.46; N, 8.61. Found: C, 40.56; H, 6.31; N, 8.52.

1,3-Di-*n*-butylimidazolium perchlorate [bbim] ClO_4: viscous oil (10.55 g; yield 98%); IR (KBr) ν = 3603, 3146, 2936, 1565, 1466, 1166, 1091, 754, 623 cm^{-1}; ^{1}H NMR δ = 0.88−0.91 (t, J = 7 Hz, 6H, CH_3), 1.29−1.36 (sept, J = 7.6 Hz, 4H, $CH_3CH_2(CH_2)_2N$), 1.80−1.85 (pent, J = 7.5 Hz, 4H, NCH_2CH_2), 4.16−4.21 (t, J = 7 Hz, 4H, NCH_2), 7.4 (s, 2H, NC*H*C*H*N), 9.02 (s, 1H, NC*H*N); ^{13}C NMR δ = 13.1, 19.1, 31.8, 49.6, 122.5, 135.3; MS *m*/*z* 181 (M − X, 100), 165 (15), 151 (12), 138 (61), 124 (40), 107 (33), 97 (65), 81 (62), 68 (16), 57 (42). Anal. Calcd for $C_{11}H_{21}N_2ClO_4$ (281): C, 46.97; H, 7.47; N, 9.96. Found: C, 46.74; H, 7.21; N, 9.82.

1-Butylimidazolium Tetrafluoroborate [Hbim]BF_4. Tetrafluoroboric acid (8.7 g, 0.1 mol) as 40% aqueous solution was added slowly over a period of 30 min to 1-butylimidazole (12.4 g, 0.1 mol) at 0 °C under stirring. The reaction mixture was stirred for an additional period of 2 h at the same temperature. Water was removed from the reaction mixture by subjecting it to evaporation for 4 h at 80 °C under reduced pressure (10 mm Hg) to give the product [Hbim]BF_4: viscous oil (19.97 g; yield 96%); IR (KBr) ν = 3607, 3153, 2876, 1580, 1466, 894, 762 cm^{-1}; ^{1}H NMR δ = 0.56 (s, 3H, CH_3), 0.95 (s, 2H, $CH_3CH_2(CH_2)_2N$), 1.47 (s, 2H, NCH_2CH_2), 3.87 (s, 2H, NCH_2), 7.12 (s, 2H, NC*H*C*H*N), 8.16 (s, 1H, NC*H*N), 14.59 (brs, 1H, NH); ^{13}C NMR δ = 13.1, 19.2, 32.1, 48.5, 120.9, 122.8, 135.2; MS: *m*/*z* 124 (M − X, 26), 109 (3), 97 (92), 81 (100), 68 (26), 55 (56). Anal. Calcd for $C_7H_{13}N_2BF_4$ (211): C, 39.81; H, 6.16; N, 13.27. Found: C, 39.81; H, 6.05; N, 13,18.

Similarly, the other ILs, viz. [Hbim]Br, [Hbim]Cl, [Hbim]PF_6, and [Hbim]ClO_4, were prepared as above using the corresponding acid of the anion.

1-Butylimidazolium bromide [Hbim]Br: viscous oil (16.20 g; yield 98%); IR (KBr) ν = 3607, 3153, 2876, 1580, 1466, 894, 762 cm^{-1}; ^{1}H NMR δ = 0.21 (s, 3H, CH_3), 0.64 (s, 2H, $CH_3CH_2(CH_2)_2N$), 1.31 (s, 2H, NCH_2CH_2), 4.03 (s, 2H, NCH_2), 7.39 (s, 1H, NC*H*C*H*N), 7.64 (s, 1H, N*H*C*H*N), 9.18 (s, 1H, NC*H*N), 12.22 (brs, 1H, NH); ^{13}C NMR δ = 13.1, 19.1, 32.4, 47.3, 120, 124.7, 136.1; MS *m*/*z* 124 (M − X, 26), 109 (3), 97 (92), 81 (100), 68 (26), 55 (56). Anal. Calcd for $C_7H_{13}N_2Br$ (206): C, 40.97; H, 6.34; N, 13.65. Found: C, 40.54; H, 6.11; N, 13,18.

1-Butylimidazolium chloride [Hbim]Cl: viscous oil (12.72 g; yield 98%); IR (KBr) ν = 3607, 3153, 2876, 1580, 1466, 894, 762 cm^{-1}; ^{1}H NMR δ = 0.48 (s, 3H, CH_3), 0.88 (s, 2H, CH_3CH_2 $(CH_2)_2N$), 1.42 (s, 2H, NCH_2CH_2), 4 (s, 2H, NCH_2), 7.11 (s, 1H, NC*H*C*H*N), 7.47 (s, 1H, N*H*C*H*N), 8.69 (s, 1H, NC*H*N), 12.17 (brs, 1H, NH); ^{13}C NMR δ = 11.7, 17.7, 30.9, 45.7, 118.3, 123.7, 134.7; MS *m*/*z* 124 (M − X, 26), 109 (3), 97 (92), 81 (100), 68 (26), 55 (56). Anal. Calcd for $C_7H_{13}N_2Cl$ (161): C, 52.17; H, 8.07; N, 17.39. Found: C, 52.08; H, 8; N, 17.28.

1-Butylimidazolium hexaflouorphosphate [Hbim]PF_6: viscous oil (21.25 g; yield 98%); IR (KBr) ν = 3607, 3153, 2876, 1580, 1466, 894, 762 cm^{-1}; ^1H NMR δ = 0.42 (s, 3H, CH_3), 0.84 (s, 2H, $CH_3CH_2(CH_2)_2N$), 1.43 (s, 2H, NCH_2CH_2), 3.96 (s, 2H, NCH_2), 7.18 (s, 2H, NC*H*C*H*N), 8.56 (s, 1H, NC*H*N), 12.61 (brs, 1H, NH); ^{13}C NMR δ = 12.6, 18.5, 31.1, 48.7, 119.5, 121.2, 133.7; MS *m*/*z* 124 (M − X, 26), 109 (3), 97 (92), 81 (100), 68 (26), 55 (56). Anal. Calcd for $C_7H_{13}N_2PF_6$ (269): C, 31.26; H, 4.83; N, 10.40. Found: C, 31.10; H, 4.71; N, 10.18.

1-Butylimidazolium perchlorate [Hbim]ClO_4: viscous oil (17.78 g; yield 98%); IR (KBr) ν = 3607, 3153, 2876, 1580, 1466, 894, 762 $cm^{-1;}$ ^1H NMR δ = 0.71 (t, *J* = 7.0 Hz, 3H, CH_3); 1.17 (sept, *J* = 7.6 Hz, 2H, $CH_3CH_2(CH_2)_2N$), 1.73 (pent, *J* = 7.5 Hz, 2H, NCH_2CH_2), 4.16 (t, *J* = 7.0 Hz, 2H, NCH_2), 7.15 (s, 1H, NC*H*C*H*N), 7.42 (s, 1H, N*H*C*H*N), 8.57 (s, 1H, NC*H*N), 11.83 (brs, 1H, NH); ^{13}C NMR δ = 12.6, 18.5, 31.1, 48.7, 119.5, 121.2, 133.7; MS *m*/*z* 124 (M − X, 26), 109 (3), 97 (92), 81 (100), 68 (26), 55 (56). Anal. Calcd for $C_7H_{13}N_2ClO_4$ (225): C, 37.33; H, 5.77; N, 12.44. Found: C, 37.10; H, 5.61; N, 12.18.

Preparation of Quinolines and Polyheterocycles. General Procedure for 3a−v. A mixture of *o*-amino-substituted ketones (**1a** or **1b,** 1 mol), ketone (**2,** 1 mol), and [Hbim]BF_4 (1 mol) was heated at 100 °C with good stirring for the appropriate time mentioned in Table 2. The completion of reaction was monitored by TLC using eluent 20% ethyl acetate in petroleum ether. After completion of the reaction, the reaction mixture was diluted with water (25 mL). The solid quinoline product which separated out was filtered, washed with water, and dried. The quinolines which are liquids were extracted with ethyl acetate (2 × 10 mL) and dried over sodium sulfate, and the solvent was evaporated under reduced pressure to furnish crude product. The crude products, thus isolated, were pure (single spot on TLC). They were subjected to further purification by chromatography through a column of silica gel using 20% EtOAc in petroleum ether as eluent to yield the desired substituted quinolines in an average 85−96% and were fully characterized.

The aqueous layer consisting of the IL was subjected to distillation (80 °C at 10 mm Hg) for 2 h to remove water, leaving behind the IL [Hbim]BF_4 (recovery 98%), which was recycled.

2,4-Dimethylquinoline-3-carboxylic acid ethyl ester (3a): oil; IR (KBr) ν = 3070, 2930, 2873, 1725, 1614, 1589, 1214, 1082, 578 cm^{-1}; ^1H NMR δ = 1.8 (t, *J* = 7 Hz, 3H), 3 (s, 3H), 3.1 (s, 3H), 4.8 (q, *J* = 7 Hz, 2H), 7.8−8.4 (m, 4H); ^{13}C NMR δ = 14.1, 15.4, 23.6, 61.4, 123.8, 125.7, 126.1, 127.9, 129.2, 129.8, 141.2, 147, 154.2, 168.9; MS *m*/*z* 230 (M^+, 100), 158 (18). Anal. Calcd for $C_{14}H_{15}NO_2$ (230): C, 73.34; H, 6.59; N, 6.11. Found: C, 73.12; H, 6.48; N, 6.05.

1-(2,4-Dimethylquinolin-3-yl)ethanone (3b): oil; IR (KBr) ν = 3068, 2959, 1703, 1614, 1585, 1208, 758 cm^{-1}; ^1H NMR δ = 2.57 (s, 3H), 2.58 (s, 3H), 2.62 (s, 3H), 7.53−8.01 (m, 4H); ^{13}C NMR δ = 15, 23.3, 32.4, 123.5, 126.2, 129, 129.6, 135.6, 138.4, 146.7, 152.4, 206.3; MS *m*/*z* 200 (M^+, 100), 158 (11), 125 (4). Anal. Calcd for $C_{13}H_{13}NO$ (200): C, 78.38; H, 6.58; N, 7.03. Found: C, 78.12; H, 6.48; N, 6.85.

9-Methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3c): mp 60 °C; IR (KBr) ν = 3065, 2957, 1613, 908, 751 cm^{-1}; ^1H NMR δ = 2.2 (m, 2H), 2.5 (s, 3H), 3 (t, *J* = 7.5 Hz, 2H), 3.3 (t, *J* = 6.9 Hz 2H), 7.46−8 (m, 4H); ^{13}C NMR δ = 14.6, 22.7, 29.4, 34.8, 123.1, 125, 126.9, 127.8, 128.9, 133.7, 137.8, 147.2, 166.7; MS *m*/*z* 183 (M^+, 40), 168 (100), 154 (5), 140 (5), 127 (10), 115 (13), 102 (5), 90 (18), 77 (91), 63 (9), 57 (3). Anal. Calcd for $C_{13}H_{13}N$ (183): C, 85.21; H, 7.15; N, 7.64. Found: C, 85.12; H, 6.98; N, 7.55.

9-Methyl-1,2,3,4-tetrahydroacridine (3d): mp 78 °C; IR (KBr) ν = 3068, 2935, 1614, 1581, 1350, 755 cm^{-1}; ^1H NMR δ = 1.73 (m, 4H), 2.25 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 7.24−7.83 (m, 4H); ^{13}C NMR δ = 12.9, 22.3, 22.7, 26.5, 33.9, 122.8, 124.7, 126.4, 127.6, 128.4, 140.7, 145.4, 157.9; MS *m*/*z* 198 (M^+, 87), 125 (100). Anal. Calcd for $C_{14}H_{15}N$ (198): C, 85.24; H, 7.66; N, 7.10. Found: C, 85.12; H, 6.58; N, 7.05.

11-Methyl-7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoline (3e): mp 108 °C; IR (KBr) ν = 3073, 2928, 1645, 1215, 755 cm^{-1}; ^1H NMR δ = 1.61−1.79 (m, 6H), 2.54 (s, 3H), 2.90 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 6.9 Hz, 2H), 7.39−7.90 (m, 4H); ^{13}C NMR δ = 14.3, 27.1, 28, 31.9, 40.1, 124, 125.7, 128.1, 129.3, 134.4, 139.3, 145.8, 164.5; MS *m*/*z* 212 (M^+, 100), 158 (2). Anal. Calcd for $C_{15}H_{17}N$ (212): C, 85.26; H, 8.11; N, 6.63. Found: C, 85.12; H, 8.15; N, 6.55.

7-Methyl-5,6-dihydrobenzo[*c*]acridine (3f): mp 112 °C; IR (KBr) ν = 3070, 3018, 2946, 2842, 1680, 1582, 1499, 1215, 758 cm^{-1}; ^1H NMR δ = 2.56 (s, 3H), 2.90 (t, *J* = 7 Hz, 2H), 3.03 (t, *J* = 6.8 Hz, 2H), 7.17−8.49 (m, 8H); ^{13}C NMR δ = 13.6, 25, 27.8, 123.3, 125.2, 126.1, 126.9, 127.4, 128, 128.9, 129.1, 129.9, 133.1, 134.9, 138.8, 139.4, 146.6, 152.3; MS *m*/*z* 246 (M^+, 100), 212 (3), 125 (31). Anal. Calcd for $C_{18}H_{15}N$ (246): C, 88.13; H, 6.16; N, 5.71. Found: C, 88.12; H, 6.09; N, 5.63.

2,3,4-Trimethylquinoline (3g): mp 110 °C; IR (KBr) ν = 3070, 2927, 1523, 1497, 1373, 1216, 753 cm^{-1}; ^1H NMR δ = 2.41 (s, 3H), 2.6 (s, 3H), 2.71 (s, 3H), 7.46−7.99 (m, 4H); ^{13}C NMR δ = 14.2, 15.6, 24.6, 123.3, 125.2, 127.7, 129.1, 140.3, 145.8, 158.2; MS *m*/*z* 172 (M^+, 100), 158 (24), 60 (4). Anal. Calcd for $C_{12}H_{13}N$ (172): C, 84.17; H, 7.65; N, 8.18. Found: C, 84.12; H, 7.59; N, 8.13.

2,4-Dimethyl-3-benzylquinoline (3h): mp 143 °C; IR (KBr) ν = 3064, 3017, 2932, 1604, 1586, 1494, 1216, 755 cm^{-1}; ^1H NMR δ = 2.53 (s, 3H), 2.57 (s, 3H), 4.2 (s, 2H), 6.93−7.95 (m, 9H); ^{13}C NMR δ = 14.3, 24.3, 35, 123.6, 125.4, 126, 127.1, 127.7, 128.4, 128.7, 129.1, 129.7, 138.7, 141.8, 146.2, 158.7; MS *m*/*z* 262 (M^+, 3), 248 (100), 125 (27). Anal. Calcd for $C_{18}H_{17}N$ (262): C, 87.41; H, 6.93; N, 5.66. Found: C, 87.12; H, 6.89; N, 5.63.

4-Methyl-2-phenylquinoline (3i): oil; IR (KBr) ν = 3061, 2958, 1684, 1265, 770 cm^{-1}; ^1H NMR δ = 2.51 (s, 3H), 7.35−8.08 (m, 10H); ^{13}C NMR δ = 18.8, 119.6, 123.6, 126, 127.5, 128, 128.3, 128.5, 128.7, 129.2, 133, 137.2, 139.8, 144.7, 148.2, 156.9; MS *m*/*z* 220 (M^+, 100), 125 (19). Anal. Calcd for $C_{16}H_{13}N$ (220): C, 87.64; H, 5.98; N, 6.39. Found: C, 87.12; H, 5.89; N, 6.33.

2-(4-Chlorophenyl)-4-methylquinoline (3j): mp 75 °C; IR (KBr) ν = 3019, 1685, 1597, 1215, 757 $cm^{-1;}$ ^1H NMR δ = 2.5 (s, 3H), 7.3−8.08 (m, 9H); ^{13}C NMR δ = 18.7, 119, 123.4, 126, 127.1, 128.6, 129.5, 130.1, 135.2, 138, 139.3, 146, 147.9, 155.4; MS *m*/*z* 254 (M^+, 86), 248 (8), 198 (100), 181 (6), 125 (50), 110 (13). Anal. Calcd for $C_{16}H_{12}ClN$ (245): C, 75.74; H, 4.77; N, 5.52. Found: C, 75.68; H, 4.71; N, 5.48.

2-(4-Bromophenyl)-4-methylquinoline (3k): oil; IR (KBr) ν = 3019, 1685, 1597, 1215, 757 cm^{-1}; ^1H NMR δ = 2.24 (s, 3H), 7.21−7.85 (m, 9H); ^{13}C NMR δ = 18.7, 118.9, 123.6, 126, 126.3 127.1, 128.8, 129.6, 130.1, 131.6, 135.7, 138.3, 144.8, 147.9, 155.3; MS *m*/*z* 298 (M^+, 100), 220 (4), 181 (6), 125 (42). Anal. Calcd for $C_{16}H_{12}BrN$ (298): C, 64.45; H, 4.06; N, 4.70. Found: C, 64.39; H, 4.10; N, 4.66.

6-Chloro-2-methyl-4-phenyl-uinoline-3-carboxylic acid ethyl ester (3l): mp 108 °C; IR (KBr) ν = 3064, 2983, 1725, 1605, 1224, 907, 732 cm^{-1}; ^1H NMR δ = 0.92−0.95 (t, *J* = 7 Hz, 3H), 2.73 (s, 3H), 4.03−4.07 (q, *J* = 7 Hz 2H), 7.32−8 (m, 8H); ^{13}C NMR δ = 13.5, 23.6, 61.4, 125.1, 125.9, 128.4, 128.7, 129.2, 130.5, 131, 132.3, 135, 145.3, 146, 154, 168; MS: *m*/*z* 325 (M^+, 77), 296 (10), 280 (100), 252 (35), 217 (63), 189 (22), 176 (53), 149 (53), 123 (13), 109 (19), 88 (19), 71 (19), 57 (33). Anal. Calcd for $C_{20}H_{19}ClNO_2$(325): C, 70.05; H, 4.95; N, 4.30. Found: C, 70.09; H, 4.90; N, 4.36.

1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)ethanone (3m): mp 151 °C; IR (KBr) ν = 3029, 2960, 1701, 1606, 1567, 1481, 909, 692 cm^{-1}; ^1H NMR δ = 1.98 (s, 3H), 2.66 (s, 3H), 7.32−7.98 (m, 8H); ^{13}C NMR δ = 23.6, 31.6, 124.7, 125.8, 128.8, 129.1, 129.8, 130.8, 132.3, 134.5, 135.4, 142.9, 145.8, 153.8, 204.9; MS *m*/*z* 295 (M^+, 41), 280 (100), 252 (29), 217 (48), 189 (15), 176 (47), 149 (27), 109 (11), 94 (9), 75 (7). Anal.

Calcd for $C_{18}H_{14}ClNO$ (295): C, 73.10; H, 4.77; N, 4.74. Found: C, 73.0; H, 4.60; N, 4.66.

7-Chloro-9-phenyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3n): mp 105 °C; IR (KBr) ν = 3060, 2958, 1606, 1487, 828, 715 cm^{-1}; ^1H NMR δ = 2.12 (m, 2H), 2.87 (t, J = 7.2 Hz, 2H), 3.19 (t, J = 7 Hz, 2H), 7.3−7.98 (m, 8H); ^{13}C NMR δ = 23.3, 30.2, 35, 124.4, 126.9, 128.2, 128.6, 129, 130.3, 131.2, 134.3, 135.9, 141.8, 146.3, 167.7; MS *m*/*z* 279 (M^+, 80), 244 (100), 202 (16), 167 (19), 121 (52), 114 (17), 94 (10), 87 (5), 75 (6), 63 (5). Anal. Calcd for $C_{18}H_{14}ClN$ (279): C, 77.28; H, 5.04; N, 5.01. Found: C, 77.19; H, 4.94; N, 4.86.

7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3o): mp 163 °C; IR (KBr) ν = 3060, 2944, 1604, 1572, 1481, 1215, 703 cm^{-1}; ^1H NMR δ = 1.55 (m, 2H), 1.59 (m, 2H), 2.56 (t, J = 6.5 Hz, 2H), 3.3 (t, J = 7 Hz, 2H), 7.2−8 (m, 8H); ^{13}C NMR δ = 23, 28.2, 34.3, 124.6, 127.5, 128.2, 128.9, 129.1, 129.3, 129.5, 130.2, 131.3, 136.5, 144.8, 145.8, 159.6; MS *m*/*z* 293 (M^+, 100), 278 (9), 258 (83), 242 (14), 230 (20), 201 (15), 189 (11), 176 (6), 150 (8), 89 (8), 77 (48). Anal. Calcd for $C_{19}H_{16}ClN$ (293): C, 77.68; H, 5.49; N, 4.77. Found: C, 77.59; H, 5.34; N, 4.68.

2-Chloro-11-phenyl-7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoline (3p): mp 175 °C; IR (KBr) ν = 3063, 2955, 1603, 1560, 1482, 907, 707 cm^{-1}; ^1H NMR δ = 0.93 (m, 2H), 1.26 (m, 2H), 1.56 (m, 2H), 2.67 (t, J = 7 Hz, 2H), 3.27 (t, J = 7.3 Hz, 2H), 7.1−7.97 (m, 8H); ^{13}C NMR δ = 26.8, 28.3, 30.6, 31.8, 40, 125, 127.8, 127.9, 128.5, 128.9, 129.2, 130.1, 131.2, 132.4, 134.8, 136.8, 144.1, 144.6, 165; MS *m*/*z* 307 (M^+, 100), 292 (16), 278 (36), 253 (11), 241 (41), 216 (17), 203 (10), 189 (13), 176 (8), 167 (16), 149 (54), 126 (29), 95 (31), 82 (30), 71 (35), 57 (35). Anal. Calcd for $C_{20}H_{18}ClN$ (307): C, 77.04; H, 5.89; N, 4.55. Found: C, 76.95; H, 5.74; N, 4.46.

9-Chloro-7-phenyl-5,6-dihydrobenzo[*c*]acridine (3q): mp 130 °C; IR (KBr) ν = 2960, 2860, 1600, 1488, 704 cm^{-1}; ^1H NMR δ = 2.86 (m, 4H), 7.25−8.61 (m, 12H); ^{13}C NMR δ = 26.4, 28, 124.8, 126.3, 127.2, 127.4, 127.9, 128.4, 128.7, 129.1, 129.3, 129.8, 130.9, 131.1, 131.6, 132.4, 136.1, 139.2, 144.5, 145.5, 153.3, 167.7; MS *m*/*z* 341 (M^+, 10), 279 (11), 167 (30), 149 (100), 104 (13), 77 (37). Anal. Calcd for $C_{23}H_{16}ClN$ (341): C, 80.81; H, 4.72; N, 4.10. Found: C, 80.65; H, 4.64; N, 4.

6-Chloro-2,3-dimethyl-4-phenylquinoline (3r): mp 127 °C; IR (KBr) ν = 3063, 2954, 1605, 1484, 1215, 755 cm^{-1}; ^1H NMR δ = 1.96 (s, 3H), 2.52 (s, 3H), 6.99−7.75 (m, 8H); ^{13}C NMR δ = 16.9, 24.4, 124.8, 127.6, 128, 128.7, 128.9, 129.2, 130.1, 131.2, 136.8, 144.4, 145.5, 159.2; MS *m*/*z* 268 (M^+, 100), 254 (18), 227 (19), 174 (75). Anal. Calcd for $C_{17}H_{14}ClN$ (268): C, 76.26; H, 5.27; N, 5.23. Found: C, 76.15; H, 5.14; N, 5.1.

3-Benzyl-6-chloro-2-methyl-4-phenylquinoline (3s): mp 136 °C; IR (KBr) ν = 3063, 2957, 1603, 1482, 1215, 756 cm^{-1}; ^1H NMR δ = 2.51 (s, 3H), 3.92 (s, 2H), 6.81−7.93 (m, 13H); ^{13}C NMR δ = 24.3, 36, 125.1, 126, 127.8, 128.2, 128.4, 129, 129.5, 130.1, 131.4, 136.2, 139.4, 144.9, 146.9, 159.7; MS *m*/*z* 344 (M^+, 100), 254 (16), 125 (4). Anal. Calcd for $C_{23}H_{18}ClN$ (344): C, 80.34; H, 5.28; N, 4.07. Found: C, 80.25; H, 5.18; N, 4.

6-Chloro-2,4-diphenylquinoline (3t): mp 102 °C; IR (KBr) ν = 3056, 1684, 1483, 908, 730 cm^{-1}; ^1H NMR δ = 7.4−8 (m, 14H); ^{13}C NMR δ = 120, 124.4, 126.4, 127.5, 128.7, 128.8, 129.4, 130.4, 131.6, 132.7, 137.7, 139.1, 147.2, 148.4, 157; MS *m*/*z* 316 (M^+, 29), 288 (100), 125 (8). Anal. Calcd for $C_{21}H_{14}ClN$ (316): C, 79.87; H, 4.47; N, 4.44. Found: C, 79.79; H, 4.38; N, 4.38.

6-Chloro-2-(4-chlorophenyl)-4-phenylquinoline (3u): mp 161 °C; IR (KBr) ν = 3019, 1588, 1215, 755 cm^{-1}; ^1H NMR δ = 7.48−8.15 (m, 13H); ^{13}C NMR δ = 119.5, 124.5, 126.5, 128.7, 128.8, 129, 129.4, 130.6, 131.7, 132.4, 135.8, 137.5, 147.2, 148.7, 155.7; MS *m*/*z* 349 (M^+, 100), 314 (40), 278 (15), 236 (16), 201 (21), 176 (19), 157 (26), 139 (52), 125 (28), 112 (8), 87 (5), 75 (14), 63 (5). Anal. Calcd for $C_{21}H_{13}Cl_2N$ (349): C, 72.01; H, 3.74; N, 4. Found: C, 71.95; H, 3.68; N, 3.92.

6-Chloro-2-(4-bromophenyl)-4-phenylquinoline (3v): mp 195 °C; IR (KBr) ν = 3018, 2928, 1645, 1580, 1215, 755 cm^{-1}; ^1H NMR δ = 7.55−8.11 (m, 13H); ^{13}C NMR δ = 119.4, 124.2, 124.5, 126.5, 128.2, 128.8, 129, 129.3, 129.8, 132, 132.5, 135.9, 137.5, 137.9, 147, 148.8, 155.6; MS *m*/*z* 394 (M^+, 20), 300 (22), 288 (72), 242 (14), 230 (12), 200 (100), 125 (27). Anal. Calcd for $C_{21}H_{13}BrClN$ (394): C, 63.91; H, 3.32; N, 3.55. Found: C, 63.85; H, 3.28; N, 3.32.

Acknowledgment. S.S.P. thanks CSIR, New Delhi, for providing a Junior Research Fellowship. We also acknowledge financial assistance from Department of Science and Technology (DST), New Delhi, Project No. SR/S5/OC-23/2002).

Supporting Information Available: ^1H and ^{13}C NMR data for compounds **3a**−**v** and for all ionic liquids (ILs) synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035153U