Taylor & Francis
Taylor & Francis Group

Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

Studies on –SO_3H Functionalized Brønsted Acidic Imidazolium Ionic Liquids (ILs) for One-Pot Two Step Synthesis of 2-styrylquinolines

Parishmita Sarma, Susmita Saikia & Ruli Borah

To cite this article: Parishmita Sarma, Susmita Saikia & Ruli Borah (2016): Studies on –SO_3H Functionalized Brønsted Acidic Imidazolium Ionic Liquids (ILs) for One-Pot Two Step Synthesis of 2-styrylquinolines, Synthetic Communications, DOI: 10.1080/00397911.2016.1193754

To link to this article: http://dx.doi.org/10.1080/00397911.2016.1193754

Studies on –SO_3H Functionalized Brønsted Acidic Imidazolium Ionic Liquids (ILs) for One-Pot Two Step Synthesis of 2-Styrylquinolines

Parishmita Sarma[1], Susmita Saikia[1], Ruli Borah[1]

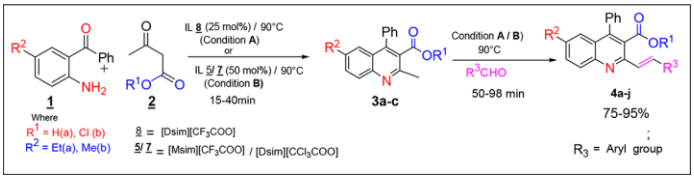
[1]Department of Chemical Sciences, Tezpur University, Assam, India

E-mail :ruli@tezu.ernet.in

Abstract

Four task-specific –SO_3H functionalized imidazolium ionic liquids were investigated for the Brønsted acidities by Hammett functions. After knowing their thermal stabilities, the catalytic activity was observed for the preparation of 2-styrylquinolines by following a consecutive Friedländer and Knoevenagel reactions in solvent-free thermal energy. The acidity order ([Dsim][$OOCCF_3$]>[Dsim][OTs]>[Dsim][$OOCCl_3$]> [Msim][$OOCCF_3$]) of three ILs was consistent with their activity order observed in the acid-catalyzed synthesis of 2-styrylquinolines under solvent-free condition at 90° C except [Dsim][OTs]. The best catalytic activity showed by 25 mol% of [Dsim][$OOCCF_3$] IL. The less acidic ILs required 50 mol% to give good yields of 2-styrylquinolines under the optimized conditions.

Graphical Abstract



KEYWORDS: Acidic ionic liquids; Hammett plot; one-pot; Friedländer and Knoevenagel condensation; recyclable IL; 2-styryl quinoline

INTRODUCTION

Designing of one pot multistep synthetic route is a sustainable structure development method in organic synthesis [1-2]. A large numbers of individual reactions are brought about in a single vessel through various steps. It makes provision for creating complex library of small organic molecules without isolating the intermediates involve in various steps with less chemical waste and greater economic benefit[3-4]. Styrylquinolines derivatives have shown extensive potential biological activities including anti-inflammatory, antitumor, antifungal, and anti-allergic, acting as HIV-1 integrase, lipoxygenase inhibitors and leukotriene d4-antagonists [5-15].Two such derivatives, FZ41 and KHD161 (Fig.1), provide a novel and promising strategy for AIDS therapy[13-15]. Some of them are effective for the treatment of Alzheimer's disease [16]. Other applications include the design of molecular logic devices [17] and supramolecular system [18].

Several known methods are available for the direct introduction of alkyl substituent into the quinoline nucleus using organometallic compounds, active methylene compounds or Wittig reagents[19-22]. However, most of the 2-styrylquinolines are obtained from the acid or base catalyzed condensation of 2-methyl quinoline derivatives with excess amount of appropriate aldehydes in acetic anhydride at high temperature (100-140° C) which produce only moderate yields of products during longer reaction time (20h)[23]. Few modified procedures utilized microwave energy to generate the title compound in good to moderate

yield from 2-methyl quinoline using $ZnCl_2$, Ac_2O/SiO_2 as catalyst in neat conditions at high temperature [24-29].They obtained the key intermediate quinalidine from Friedländer, Doebner–von Miller,Combes, and Pfitzinger reactions[30-32]. Another two step method also describes the preparation of 2-styryl-1, 2, 3, 4-tetrahydroquinolines via a vinylogous Povarov reaction followed by aromatization which isn't yet commonly applicable in terms of the substitution on the styryl side chain [13, 33-34]. All these multistep protocols provide low yield, time consuming and produce side products.

Dabri *et al* first employed 1-methyl-imidazolium trifluoroacetate IL as acidic medium for the one pot synthesis of 2-styrylquinolines via Friedländer annulation of 2-aminoarylketone and methylketone followed by Knoevenagel reaction with aromatic aldehyde at 80° C in 2h (Scheme 1)[35]. Recently Kumar *et al* also exploited the synthesis of title compounds using this approach in presence of 10 mol% of $In(OTf)_3$ as catalyst at 100° C within 2-4 h[36]. Both methods required longer reaction time to give good to excellent results. Although the both one pot methods have several advantages such as simple work up procedure, high yields of required product, no side product, use of recyclable acidic medium/catalyst, but the major limitation is the use of stoichiometric amount of less acidic IL and longer reaction time (2-4 h). As results there is a scope to use strong acidic ILs as reusable homogeneous catalytic system for the preparation of 2-styrylquinolines.

The -SO_3H functionalized ionic liquids represent a class of strong task specific Brønsted acidic ILs and they have many applications as recyclable acid catalyst in organic reactions under mild conditions, which is rather difficult to obtain with other Lewis or Brønsted acid catalysts [37]. The acidity of such ILs can be varied with the incorporation of one or more –SO_3H groups into the cations. In this study, four acidic sulfoimidazolium ILs 3-methyl-1-sulfoimidazolium trifluoroacetate ([Msim][$OOCCF_3$]) **5 ,** 1, 3-disulfoimidazoliumtosylate ([Dsim][OTs]) **6** and 1,3-disulfo-imidazolium carboxylate ILs ([Dsim][X]) where X = [CCl_3COO]$^-$ **7**, [CF_3COO]$^-$ **8** were investigated as catalyst/medium for the preparation of **4**(Fig. 2).

RESULTS AND DISCUSSION

At first we synthesized the three known ILs ([Msim][$OOCCF_3$]) **5 ,** ([Dsim][$OOCCCl_3$]) **7** and ([Dsim][$OOCCF_3$]) **8** (Fig. 2) from the reaction of 1-sulfo-3-methylimidazolium chloride ([Msim]Cl) with CF_3COOH and 1,3-disulfo-imidazolium chloride ([Dsim]Cl) with CCl_3COOH and CF_3COOH respectively[38-39]. In next phase, we prepared ([Dsim][OTs]) **6** IL from the reaction of [Dsim]Cl with *p*-toluene sulfonic acid at room temperature (Scheme 2).

The FT-IR spectra of IL **6** indicated three absorption bands around 1208, 1048 and 582 cm^{-1} which are assigned for the stretching and bending vibrations of -SO_3H group (Fig. 3). It has another strong peak at 823 cm^{-1} corresponding to N-S stretching vibration. The ^1H NMR spectra of **6** has two proton singlet at 14.1 ppm for the –SO_3H acidic protons. The elemental analyses further confirmed the structure of the new IL ([Dsim][OTs]) **6**.

From the previous study, we knew the thermal stability of ILs **7** and **8** up to 260° C [39]. Therefore, we performed the thermal analysis of two ILs (**5**, **6**) (Fig. 4). The TGA profile of IL **5** showed slight weight loss at 67.7° C which can be assigned for the elimination of absorbed water from IL. It has higher thermal stability up to 364° C than **6, 7** and **8**. In contrast, the TGA curve of ([Dsim][OTs]) expressed 40 % decomposition at 57.5° C. The reason may be the weaker strength of ionic bond between imidazolium cation and tosylate anion in ([Dsim][OTs]) with increasing temperature and thus, the –OTs group can easily eliminate as strong leaving group in the form of *p*-toluene sulfonic acid through abstraction of acidic proton from electrophilic -N–SO_3H group of imidazolium cation. This was further confirmed from the ^{1}HNMR spectra of [Dsim][OTs] IL after heating at 60° C for one hour This spectra expressed this IL as a mixture of p-TSA and 1-sulfonic acid imidazole displaying an acidic proton at δ 14.2 ppm and two distinct doublets for four aromatic proton of p-TSA at 7.10 ppm and 7.47 ppm respectively.

Hammett function (H^o) is an effective way to measure the acidity of various acidic ionic liquids using UV-Visible spectrophotometer according to equation (1) in presence of 4-nitroaniline as weak base [40-41]. In the equation- (1), the term p*K*(I)aq represents p*K*a value of the weak base indicator in aqueous solution and [I] is the absorbance of indicator without protonation.

$$H^o = pK\ I\ aq + \log\ I\ /\ IH^+ \qquad (1)$$

The acidities of ILs were expressed in terms of Hammett function in table-1 by the extent of protonation of the indicator with the decreasing absorbance [I] of basic indicator. The

protonated form $[HI]^+$ of the indicator didn't show any absorbance due to smaller molar absorptivity. The procedure started with the mixing of basic indicator (0.04mmol /dm^3, p*K*a＝0.99) and ILs (5 mmol/dm^3) solution in ethanol with equal concentration which gave maximum absorbance at 378 nm.

The observed acidities of ILs was arranged in the decreasing trend by increasing the values of Hammett function (table-1) according to the Uv-vis plot as follows:([Dsim][$OOCCF_3$])>([Dsim][OTs]) > ([Dsim][$OOCCl_3$])>([Msim][$OOCCF_3$]) (Fig. 5).

Table-2 includes the standardization results of 2-styryl quinoline **4a** starting from 2-aminobenzophenone (1mmol), acetoacetic ester (1mmol) and *p*-tolualdehyde (1mmol) using the acidic ILs **(5/6/7/8)** as catalysts/medium at various temperature. As reaction medium, they produced 22-39 % of 2-methylquinoline **3a** at room temperature during 12 h stirring (table-2, entry-1). By increasing the temperature to 100° C, the reaction was completely converted to **3a** on TLC observation using 50 mol % of **5**/**7**/**8** ILs within 10-40 min (table-2, entry-2) except **6** which decomposed at 57.7^o C in the TGA analysis. In next step, the crude intermediate **3a** gave 84-96 % of **4a** after treatment with 1 mmol of *p*-toluadehyde at 100° C (table-2, entry-3). The three ILs formed similar yields of **4a** at 90° C (table-2, entry- 4). Among the three ILs, the best catalytic activity obtained from 25 mol % of **8** at 90° C (table-2, entries 5-6). We optimized 50 mol % of weak acidic ILs **5** and **7** as task specific reaction medium for the preparation of **4a** at 90° C (table-2, entry

4). The model reaction yielded 62-70 % of **4a** with 25 mol % of **8** in methanol and water solvents during 4 h reflux in 2nd step (table-2, entry 7).

The standard reaction conditions were expanded with various 2-aminoaryl ketones and β-keto ester and substituted aromatic aldehydes. The results were summarized in table-3. The product formation was observed to be satisfactory within 1-2 h min time in the 2nd step regardless of the nature of substituted aromatic aldehydes. The condensation reaction didn't occur with aliphatic aldehyde using IL **8** as catalyst (table-3, entry 11).

Single crystal X-ray analysis was performed on the 2-styrylquinoline derivative **4j**(table-3, entry-10) which confirmed the presence of basic 2-styrylquinoline moiety (Fig. 6) along with (*E)*-conformation of two hydrogen atoms on the styrene double bond [42].

The reusability of strong acidic ionic liquid catalyst **8** was performed up to 4th cycle for the preparation of **4a** from the mixture of 2-amino benzophenone (1 mmol), ethylacetoacetate (1 mmol) and *p*- tolualdehyde (1mmol) at 90° C and it was expressed by the bar diagram (Fig. 7).

EXPERIMENTAL SECTION

General Remarks

The ^{1}H and ^{13}C NMR spectroscopic data of all products were recorded on JEOL (400 MHz), Bruker (400 MHz) and (300 MHz) spectrometer using Me_4Si as internal standard. The NMR samples were run in $CDCl_3$ and DMSO-d_6. The coupling constants were (*J*)

expressed in Hertz (Hz). FT-IR spectra of all compounds were recorded on a Nicolet Impact-410 spectrometer. Single crystal data of compound **4j** was recorded on Bruker SMART APEX II CCD diffractometer**.** Elemental analyses of the products were performed on Perkin Elmer 20 analyzer. Melting points were determined on Buchi M-560. All products were identified by FT-IR, ^{1}H NMR, ^{13}CNMR, and melting point data and also by comparison with literature reported data[35-37].The ^{1}H NMR and ^{13}C NMR spectra of new ionic liquid and 2-styrylquinoline derivatives were included in supplimentary file.

Experimental Procedures

General Procedure For The Synthesis Of Ionic Liquids

The known three ionic liquids ([Msim][$OOCCF_3$]) **5 ,** ([Dsim][$OOCCCl_3$]) **7** and ([Dsim][$OOCCF_3$]) **8** were prepared according to the previously reported procedures[38]. The novel IL 1, 3- disulfo-imidazolium tosylate([Dsim][OTs]) **6** was synthesized by following the reaction Scheme 2. In a 50 mL two necked round bottomed flask containing 5 mmol (1.32g) of [Dsim]Cl ionic liquid, equal amount of *p*-toluene sulfonic acid (5 mmol, 0.86 g) was added over a period of 10 mins and then stirred at room temperature for 1 hour. To remove the HCl gas produced during the period, an alkali trap was connected through a vacuum system. After completion of one hour stirring, the viscous reaction mixture was washed with dry CH_2Cl_2 (25 mL) and dried under reduced pressure to give [Dsim][OTs] as colourless oil with 97 % (1.94 g) yield.

Typical Procedure For The Synthesis Of 2-Styrylquinoline Derivatives 4

A mixture of 2-aminoaryl ketone (1.0 mmol), β-keto ester (1.0 mmol) and 25 mol% of acidic ILs was heated in a 50 mL round bottom at 90° C for the specified time. After completion of the reaction as monitored by thin layer chromatography (using 1:10 ethyl acetate and petroleum ether as developing solvent) to the corresponding 2-methyl quinoline derivatives, 1 mmol of aromatic aldehyde was added to the reaction mixture. The reaction was again continued for the respective reaction time as represented in table-3 at 90° C for the formation of 2-styrylquinolines. The crude product was extracted from the ionic liquid phases using dichloromethane (2 x 3 mL) as solvent which was isolated from the dichloromethane solution after distillation under reduced pressure. The catalyst ionic liquid was retained as viscous layer in the reaction vessel and it was again utilized for next cycle of reaction. Further purification of the solid product was completed by recrystallization from ethanol to get analytically pure product.

Spectral Data Of New Ionic Liquid And 2-Styrylquinoline Derivatives

1, 3- disulfo-imidazolium tosylate [Dsim][OTs] ***6****(new)*: FT-IR(KBr): 3464, 1638, 1208, 1048, 823, 688, 582, 478, 418 cm^{-1} ; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.11(s, 3H), 7.04(s, 2H), 7.46-7.50 (m, 4H), 8.91(s, 1H), 14.13(s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 21.2, 119.8, 125.9, 129, 134.6, 139.5, 139.7,143.8,144.1.

Ethyl-2-[(E)-2-(naphthalene-3-yl)vinyl]- 4-phenyl-quinoline-3-carboxylate ***4c*** *(Table 3, Entry 3, new):* Yellow solid, Mp. 158.6-159.2° C, FT-IR (KBr) cm^{-1}:3451, 3242, 3048 ,2927, 2377, 2271, 1624, 1582, 1504, 1434, 1362, 1301, 1265, 1168, 1098, 980, 865, 821, 742;^{1}HNMR (400MHz, $CDCl_3$) δ ppm :0.92(t, *J* = 6.9Hz, 3H), 4.05(q, *J* = 6.9Hz, 2H),

7.28-7.43(m,9H), 7.52(d, *J* = 8.2Hz, 1H), 7.64-7.85(m, 5H),7.97(s, 1H), 8.18(d, *J* = 8.6 Hz, 1H), 8.26(d, *J* = 15.6Hz, 1H);^{13}CNMR(75MHz, $CDCl_3$) δ ppm : 168.2, 151.0, 148.1, 146.8, 143.4, 136.6, 135.7, 134.6, 134.1, 133.5, 130.5, 129.5, 129.4, 129.1, 128.6, 128.4, 128.3, 128.0, 127.7, 127.3, 127.0, 126.6,126.3,125.7,124.5,123.8, 123.5,61.6,13.7;CHN analysis (%) : $C_{30}H_{23}NO_2$, Cal. C 83.89, H 5.40, N 3.26; Found C 83.86, H 5.44, N 3.22.

CONCLUSION

In summary, this study has identified the catalytic activity of IL **8** among four different sulfoimidazolium BAILs for the one pot synthesis of 2-styrylquinolines after comparing their acidities and thermal stabilities. This is the first report of $–SO_3H$ functionalized ionic liquid catalyzed synthesis of 2-styrylquinoline with excellent yields at 90 °C within 1 h. The weak acidic ILs **5** and **7** promoted the reaction as reaction medium at the same temperature. The new IL **6** decomposed at 57.5° C and didn't catalyze the reaction under the optimized condition.

SUPPLEMENTARY MATERIAL

Supplemental data for this article can be accessed on the publisher's website. This file contains the spectra of 2-styryl quinolines **4** and new ionic liquid **6.**

ACKNOWLEDGEMENT

The authors are thankful to Sophisticated Analytical Instrumentation Centre, T.U. for analyses of various samples for this work and also to CSIR, New Delhi, India for granting a research project no. 02(0067)/12/EMR-II to R. B.

REFERENCES

[1]Broadwater, S. J.; Roth, S.L.; Price, K.E.; Kobaslija, M.; McQuade, D.T.*Org. Biomol. Chem*., **2005**,*3*, 2899-2906.

[2]Climent, M.J.; Corma, A.; Iborra, S.; Mifsud, M.; Velty, A. *Green Chem*. **2010**,*12*, 99-107.

[3]Nordmann, J.; Müller, T.J.J. *Org. Biomol.Chem*.**2013**, *11*, 6556- 6561.

[4] Ferguson, M.;Giri, N.; Huang, X.;Apperley, D.; James,S.L.*Green Chem.* **2014,***16*,1374-1382.

[5]Ouali, M.; Laboulais, C.;Leh,H.;Gill, D.;Desmaële, D.; Mekouar, K.; Zouhiri, F.;d'Angelo, J.;Auclair, C.;Mouscadet, J.F.; Bret,M.L.*J Med. Chem.***2000,***43*,1949-57.

[6] Normand-Bayle, M.;Bénard, C.; Zouhiri, F.;Mouscadet, J.F.; Leh, H.; Thomas, C.M.; Mbemba, G.;Desmaëlea, D.;d'Angelo, J. *Bioorg. Med. Chem. Lett.***2005**,*15*, 4019-4022.

[7] Firley, D.; Courcot, B.; Gillet, J.M.;Fraisse, B.;Zouhiri, F.;Desmaëlea, D.;d'Angelo, J. ; Ghermani, N.E. *J Phys.Chem.B.***2006,***110*, 537-547.

[8] Zouhiri, F.; Desmaëlea, D.; d'Angelo, J.; Ourevitch, M.; Mouscadet, J.F.;Leh, H.;Bretd, M.L.*Tetrahedron Lett.***2001,***42*, 8189- 8192.

[9]Gavrishova, T. N.; Li, V.M.;Sadykova, K.F.; Budyka, M.F.*Russ. Chem. Bull. Int. Ed*.,**2011,***60*, 1495-1499.

[10] Nosova, E.V.;Stupina, T.V.;Lipunova, G.N.;Charushin, V.N.*J. Fluorine Chem.***2013,***150*, 36-38.

[11] Eswaran, S.;Adhikari, A.V.; Chowdhury, I. H.; Pal, N.K.; Thomas, K.D.*Eur. J Med. Chem.***2010,***45*,3374-3384.

[12] Da Silva, A. D.; De Almeida, M.V.; De Souza, M.V.N.;Couri, M.R.C.*Curr.Med. Chem.***2003,** *10*, 21-39.

[13]Makhija, M.T.*Curr. Med. Chem*. **2006**, *13*, 2429-2441.

[14] Pommier, Y.; Johnson, A.A.; Marchand, C. *NatRev. Drug Discovery*, **2006,***4*, 236-248.

[15] d'Angelo, J.; Mouscadet, J-F.; Desmaele, D.; Zouhiri, F.; Leh, H.*Pathol. Biol.***2001,***49*, 237-246.

[16] Li, Q.; Min, J.; Ahn, Y.H.; Namm, J.; Kim, E.M.;Lui, R.; Kim, H.Y.; Ji,Y.;Wu, H.;Wisniewski,T; Chang, Y.T.*Chem.Bio.Chem.***2007,***8*,1679-1687.

[17]Budyka, M.F.; Potashova, N.I.; Gavrishova, T.N.;Li,V.M.. *J Mater. Chem.***2009,***19*,7721-7724.

[18] Budyka, M.F.; Lee,V.M.;Gavrishova, T.N.*J Photochem. Photobio.A : Chem.***2014,***279*, 59-64.

[19]Taylor, E. C.; Martin, S. F. *J Am.Chem.Soc.***1974**, *96*, 8095-8102.

[20]Ochiai, E.; Kuniyoshi, I. CXVI.Nitration of 1-benzylisoquinoline.*Pharm. Bull.***1957,***5*, 289-291.

[21] Cooper, G. H.; Rickard, R.L.*J Chem.Soc. C* :**1971,**772-776.

[22]Taylor, E. C.; Martin, S. F.*J Am. Chem. Soc.***1972**, *94*, 2874-2875.

[23]Bayle, M. N.; Benard, C.;Zouhiri, F.; Mouscadet, J-F.; Leh, H.; Thomas, C-M.; Mbemba, G.; Desmaele, D.; d'Angelo, J. *Biorg. Med. Chem. Lett.***2005**, *15*, 4019-4022.

[24] Musiol, R.; Podeszwa, B.; Finster, J.; Niedbala, H.; Polanski, J.*Monatsh. Chem.***2006**, *137*, 1211-1217**.**

[25] Li,V.M.;Gavrishova, T.N.;Budyka, M.F.*Russ. J Org. Chem*. **2012,** *48*, 826-831.

[26]Staderini, M.; Cabezas, N.; Bolognesi, M. L.; Menendez, J.C.*Synlett*, **2011**,*17*, 2577-2579.

[27]Gavrishova, T.N.; Li, V.M.; Gorkovand, K.V.; Budyka, M.F. *Russ. J Appl. Chem.***2011**, *84*,516-518.

[28] Polanski, J.; Niedbala, H.; Musiol, R.;Tabak, D.; Podeszwa, B.;Gieleciak, R.; Bak, A.;Palka, A.; Magdziarz, T.*Acta. Poloniae. Pharm. Drug Res.***2004**, *61*, 3-4.

[29] Majera-Maniecka, K. A.; Musiol, R.; Nitek, W.; Oleksyn, B.J.; Polanski, J.*Bioorg. Med. Chem. Lett.***2005**, *16*,1005-1009.

[30]Cheng, C-C.; Yan, S-J.*Org. React.***1982,***28*, 37-201.

[31]Bergstrom,F.W.*Chem. Rev.***1944**, *35*, 77-277.

[32] Jones. G. *In The Chemistry of Heterocyclic Compounds*,WeissbergerA, Taylor EC, Eds.; John Wiley and Sons: Chichester, **1977,** Vol. *32*, Part I, 93.

[33]Sridharan, V.; Avendano, C.; Menendez, J.C.*Tetrahedron***2009**, *65*, 2087-2096.

[34]Leonard, J. T.; Roy, K. *Eur. J. Med. Chem.* **2008**, *43*, 81-92.

[35] Dabiri, M.; Salehi, P.; Baghbanzadeh, M.; Nikcheh, M.S.*Tetrahedron Lett*. **2008**,*49*, 5366-5368.

[36]Kumar, D.; Kumar, A.; Qadri, M. M.; Ansari, M.I.; Gautam, A.; Chakraborti, A.K.*RSC Adv*.**2015**, *5*, 2920- 2927.

[37]Olivier-Bourbigou, H.; Magna, L.; Morvan, D. *App. Cat. A: Gen*.**2010**, *373*, 1-56.

[38] Dutta, A.K.; Gogoi, P.; Borah, R. *RSC Adv*.**2014**, *4*, 41287- 41291.

[39]Kore, R.; Kumar,T.J.D.;Srivastava, R.*J Mol. Cat. A: Chem.***2012,***360*, 61-70.

[40]Gu, Y.; Zhang, J.; Duan, Z.; Deng, Y. *Adv. Syn. Catal*.**2005**, *347*, 512-516.

[41] Binstein, S.; Devilleus, J. *Chemosphere* **1994**, *28*, 1171-1188

[42] CCDC-1053069 (for 4j) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.ac.uk./data/_request/cif.

Table 1. Calculation of the Hammett Function for various ILs in ethanol

Entry	IL	A_{max}	[I]%	[IH]%	H_0[a]
1	Blank	1.394	100.0	0	-
2	[Msim][$OOCCF_3$] **5**	0.815	58.5	41.5	1.14
3	[Dsim][$OOCCl_3$] **7**	0.798	57.2	42.8	1.12
4	[Dsim][OTs] **6**	0.743	53.3	46.7	1.05
5	[Dsim][$OOCCF_3$] **8**	0.541	38.8	61.2	0.79

[a] Indicator: 4-nitroaniline

Table 2. Optimization of the amount of ionic liquids and temperature for the synthesis of **3a** and **4**

Entry	ILs (mol %)	Temp. (° C)	Time		% Yield of products [a,b]	
			3a(min) Step I	4a(h) Step II	3a	4a
1	**5**/**6**/**7**/**8** (100)	25	12 h	—	22/35/27/39	-
2	**5**/**7**/ (50)	100	40/25/10	—	97/97/98	-
3	**5**/**7**/**8** (50)	100	40/25/10	2 /1.5/1	-	84/87/96
4	**5**/**7**/**8** (50)	90	40/30/10	2/1.5/1	-	83/85/95
5	**5**/**7**/**8** (25)	90	3 h /2.5h/15	—	70/80/97	–
6	**8**(25)	90/80	15/35	1 /85min	–	94/83

7	**8**(25)	70/100	1 h	4	82/77	70/62

[a] Reactions were carried from the 1:1 ratio of 2-amino benzophenone and ethylacetoacetate using ionic liquid (**5** /**6** /**7** /**8**) followed by addition of 1 mmol of *p*-tolualdehyde ;[b]Isolated yields.

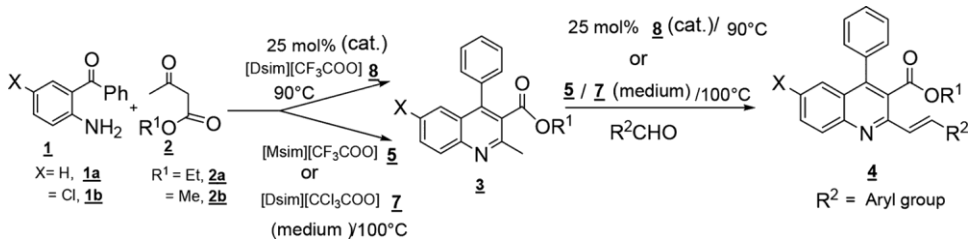
Table 3. Evaluation of the catalytic activity of ILs **5**, **7** and **8** for the synthesis of 2-styrylquinoline derivatives **4**

Entry	1	2	R^2CHO	Time (method)[a]		Product **4** Yield[b] (%) 5/7/8	Mp. **4** [reported][35] °C
				3 (min)	4 (hour)		
1	**1a**	**2a**	4-$CH_3C_6H_4$-	40(I)/30(II)/15(III)3a	2 /1.5/ 1	83/85/94 4a	150.7-152.8
2	**1a**	**2a**	4-$NO_2C_6H_4$-	**3a**	2 /1.5/ 1	81/84/904b	171.4-172.5
3	**1a**	**2a**	2-naphthyl-	**3a**	2 /1.5/ 1	80/84/884c	158.6-159.2
4	**1b**	**2b**	4-$MeOC_6H_4$-	48(I)/40(II)/20(III)3b	2 /1.5/ 1	80/83/954d	146.3-146.9°
5	**1b**	**2b**	4-HOC_6H_4-	**3b**	2 /1.5/ 1	78/81/934e	182.7-184.3
6	**1b**	**2a**	4-$MeOC_6H_4$-	50(I)/45(II)/25(III)3c	2 /1.5/ 1	75/80/924f	145.7-147.2 [147-148]
7	**1a**	**2a**	Ph-CH=CH-	**3a**	2 /1.5/ 1	81/84/904g	169.6-172.1
8	**1a**	**2a**	4-ClC_6H_4-	**3a**	2 /1.5/ 1	75/79/94 4h	150.5-154 [150-153]
9	**1a**	**2a**	4-HOC_6H_4-	**3a**	2 /1.5/ 1	80/83/934i	233-234° [232-234]

10	**1a**	**2a**	4-$MeOC_6H_4$-	**3a**	2 /1.5/ 1	83/85/954j	126.7-129
11	**1a**	**2a**	C_4H_9-	**3a** (III)	2 h	No reaction	—

[a] Method : (I) using 50 % of IL 5 at 90° C in neat (II) using 50 mol% of IL 7 at 90° C in neat (III) using 25 mol% of IL 8 at 90° C in neat ;[b] Isolated yields

Scheme 1. Preparation of 2-styrylquinoline derivatives **4**



Scheme 2. Synthesis of [Dsim][OTs] ionic liquid

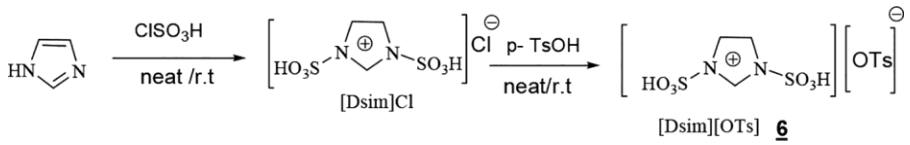
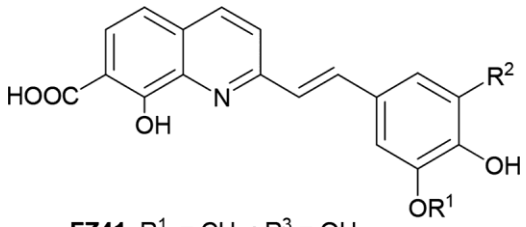


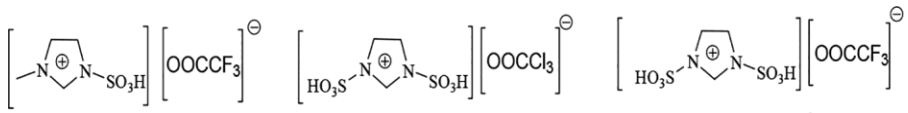
Figure 1. Structure of FZ41 and KHD161 as 2-stryrylquinoline derivatives



FZ41 $R^1 = CH_3$; $R^3 = OH$

KHD161 $R^1 = H$; $R^2 = H$

Figure 2. Structure of three sulfoimidazolium BAILs



[Msim][$OOCCF_3$] **5** [Dsim][$OOCCl_3$] **7** [Dsim][$OOCCF_3$] **8**

Figure 3. FT-IR spectra of IL **6**

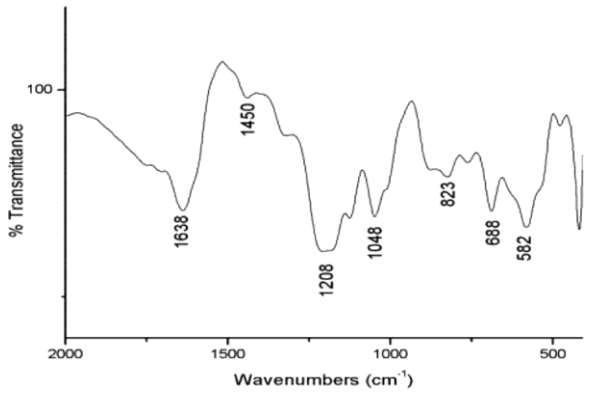


Figure 4. TGA and DTGA analysis of the ionic liquids **5** and **6**

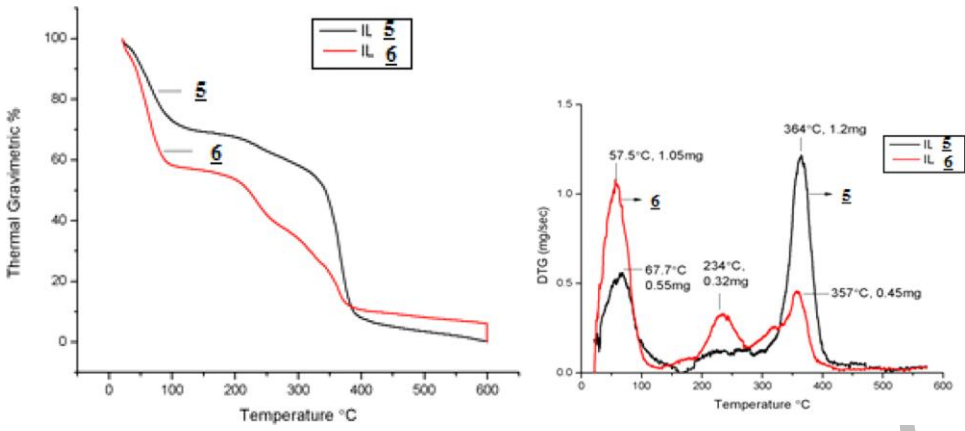


Figure 5. Absorption spectra of basic indicator

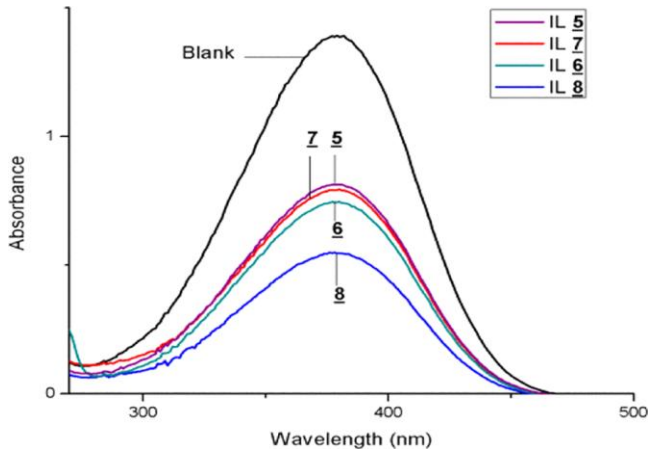


Figure 6. Single crystal structure of **4j**. The displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii

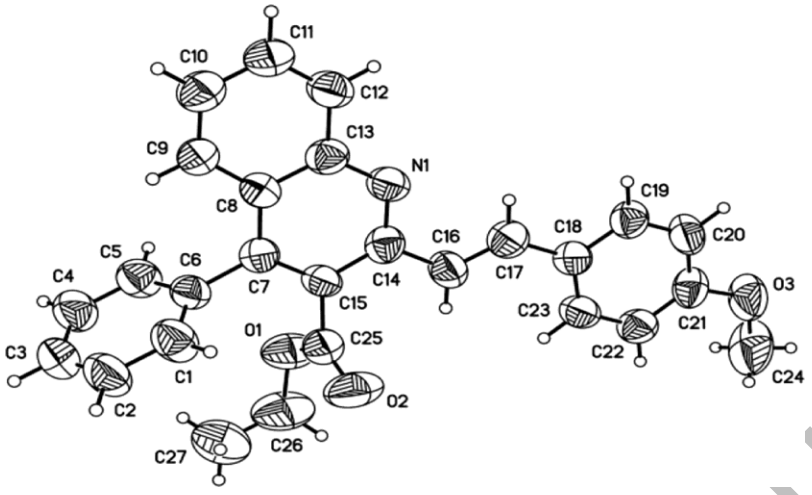


Figure 7. Reusability of IL **8** as catalyst for the preparation of **4a**