Novel SO₃H-functionalized ionic liquids catalyzed a simple, green and efficient procedure for Fischer indole synthesis in water under microwave irradiation

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ABSTRACT

Novel SO₃H-functionalized ionic liquids were successfully applied as catalysts for one-pot Fischer indole synthesis under microwave irradiation and in a water medium. Various types of indoles were prepared using single-carbonyl ketones/aldehydes or cyclohexandiones with aryhydrazine hydrochlorides in 86–96% yields in water under microwave irradiation. The indole products could be conveniently separated from the reaction mixture through filtration, and the catalytic system of $[(HSO_3-p)_2im][CF_3SO_3]/H_2O$ could be reused directly without any treatment. The entire process is simple, time saving, and environmentally friendly.

1. Introduction

The indole ring system is probably the most ubiquitous heterocycle that represents an important structural component in many pharmacologically active compounds, agrochemistry and materials science [1]. Although many methods have been developed for the synthesis of indoles [2], compared with other methodologies for indole synthesis, the Fischer indole synthesis through the reaction of ketones with aryhydrazines remains an extremely useful and important method [3]. Since its discovery in the 1880s by Emil Fischer, various catalysts have been used to effect the cyclization of enolizable N-arylhydrazones derived from ketones and arylhydrazones. As the catalysts for the Fischer indole synthesis, Brønsted acids (H_2SO_4, HCl, PPA, AcOH, and TsOH) [4], Lewis acids ($ZnCl_2$ and $TiCl_4$) [5], and solid acids (zeolite and montmorillonite clay) [6], have been reported. The reported Brønsted and Lewis acids are environmentally unfriendly, hazardous, difficult to reuse, and usually required large amounts. Solid acids have shortcomings as well. Among the more troublesome of these are restricted accessibility of the matrix-bound acidic sites, high molecular weight/active-site ratios, and rapid deactivation from coking. Thus, despite a varity of synthetic routes developed so far, a more concise, environmentally friendly one-pot option that eliminates the potential hazards is desirable.

Acidic ionic liquids have been reported as a new class of promising compounds for the development of environmentally friendly acidic catalysts owing to the combination of the advantages of liquid acids and ionic liquids (ILs) [7]. Rebeiro and Khadikar firstly described the synthesis of indoles using the ionic liquid 1-butyl-pyridinium chloride·3AlCl₃ as a dual solvent-catalyst [8a]. Jenkins et al. carried out the Fischer indole synthesis using one equivalent of the IL choline chloride·2ZnCl₂ for the exclusive formation of 2,3-disubstituted indoles [8b].

These Lewis acidic ILs present excellent catalytic activities. However, their application was limited because they are unstable in air and difficult to reuse. Our previous work described the synthesis of indoles with [bmim][HSO₄] and successfully conquered some of the drawbacks mentioned above. Moreover, we found that the acidity of the ILs is an important property relevant to their catalytic activity for the indole synthesis [8c]. In 2009, we investigated the catalytic ability of acidic ILs in the Fischer indole synthesis. For enhancing the acidity and catalytic performance of these ILs, novel SO₃H-functionalized ILs with two alkyl sulfonic acid groups in imidazolium cations were designed and applied for indole synthesis in water (Fig. 1) [9]. The developed methodology is convenient and could afford good to excellent yields. Moreover, water could be used as a solvent, and the catalyst could be reused. However, an important drawback of the aforementioned methodologies lies in the 1.0 equivalent NH₃ produced in the reaction, which can reduce the catalytic activity and decrease the yield. Water and HCl (or the strongly acidic cation exchange resin Dowex-50) must be used in the reaction–recycle process to maintain its catalytic ability and reuse the Brønsted acidic ILs.
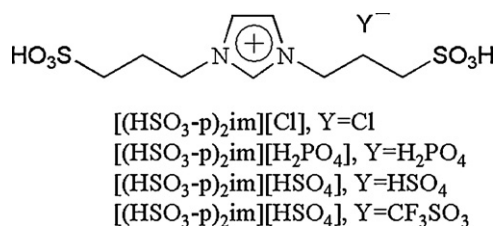
Fig. 1. Novel Brønsted acidic ILs bearing two alkyl sulfonic acid groups.

Scheme 1. Synthesis of the novel Brønsted acidic ILs.

These procedures make the operation slightly complicated and require a long reaction time (0.5–6 h) along with a high loading of ILs (about 0.5 equivalent).

In recent years, organic reactions under microwave irradiation (condition) have become popular because of their higher reaction rates, simpler operation, and more safe and environmentally friendly reaction conditions. In contrast to well-studied approaches for the Fischer indole syntheses from aryhydrazines derivatives, the use of aryhydrazine hydrochlorides has received far less attention. Moreover, aryhydrazine hydrochlorides are readily available, safe, low-toxic, and cheap substrates suitable for the Fischer indole synthesis [10a,b]. These substrates offer a more green, practical, and scalable method for the large-scale preparation of indoles. In the present work, we investigated the
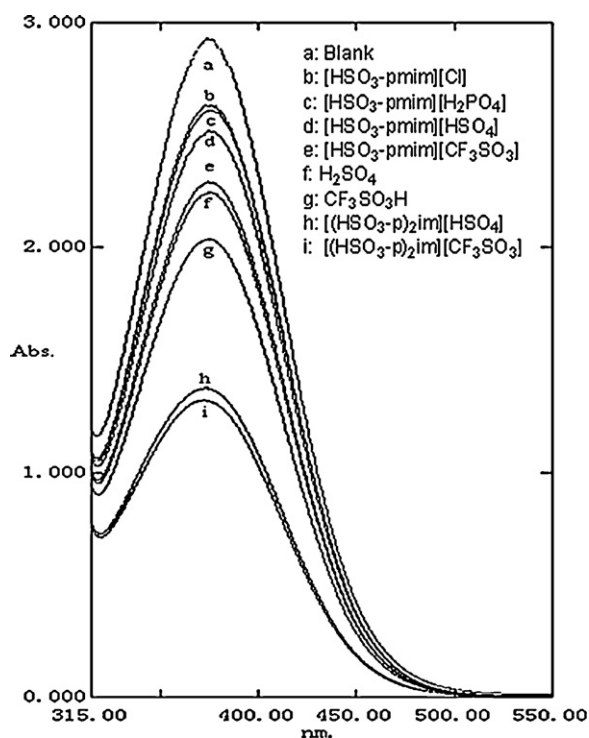

Scheme 2.

Microwave-assisted Fischer indole synthesis from aryhydrazine hydrochlorides in a water medium.

2. Results and discussion

Novel SO_3H-functionalized acidic ILs bearing two alkyl sulfonic acid groups were prepared from the reaction of N-trimethylsilyli-midazole with 1,3-propane sultone, followed by the acidification of the afforded zwitter ion compound with strong acids (Scheme 1) [9]. Because the acidity of the ILs is an important property related to their catalytic activity for the indole synthesis. Thus, it encouraged us to further explore the catalytic activity of imidazolium salts using trifluoromethanesulfonate anion for the counter anion. The Brønsted acidity of above typical ILs was evaluated from the determination of the Hammett acidity functions using UV–vis spectroscopy with 3-nitroanline as the indicator in ethanol [11]. As shown in Fig. 2, the maximum absorbance of the unprotonated form of the indicator was observed at 374 nm, which decreased on adding acids. The decreasing order of the absorbance of acids and ILs was observed as follows: [HSO_3-pmim][Cl] > [HSO_3-pmim][H_2PO_4] > [HSO_3-pmim][HSO_4] > [HSO_3-pmim][CF_3SO_3] > H_2SO_4 > CF_3SO_3H > [(HSO_3-p)$_2$im][HSO_4] > [(HSO_3-p)$_2$im][CF_3SO_3], indicating the acidity order as follows: [(HSO_3-p)$_2$im][CF_3SO_3] > [(HSO_3-p)$_2$im][HSO_4] > CF_3SO_3H > H_2SO_4 > [HSO_3-pmim][CF_3SO_3] > [HSO_3-pmim][HSO_4] > [HSO_3-pmim][H_2PO_4] > [HSO_3-pmim][Cl].

Table 1
Microwave-assisted Fischer indole synthesis catalyzed by different ILs and acids in water.[a]

Entry	Acidic catalyst	Time/min	Isolated yield (%)[g]
1	Ceric ammonium nitrate (CAN)	20	30
2	p-TsOH	20	35
3[b]	HCl	15	77
4	H_3PO_4	15	70
5[b]	H_2SO_4	15	84
6	CF_3SO_3H	15	85
7	[HSO_3-pmim][Cl]	15	30
8	[HSO_3-pmim][H_2PO_4]	15	75
9	[HSO_3-pmim][HSO_4]	15	77
10	[HSO_3-pmim][CF_3SO_3]	15	78
11[b]	[(HSO_3-p)$_2$im][HSO_4]	15	93
12[b]	**[(HSO_3-p)$_2$im][CF_3SO_3]**	**15**	**96**
13[c]	[(HSO_3-p)$_2$im][CF_3SO_3]	15	95
14[b,d]	[(HSO_3-p)$_2$im][CF_3SO_3]	15	92
15[b]	[(HSO_3-p)$_2$im][CF_3SO_3]	10	89
16[b,e]	[(HSO_3-p)$_2$im][CF_3SO_3]	60	80
17[b,f]	[(HSO_3-p)$_2$im][CF_3SO_3]	15	50

Reaction conditions:
[a] Cyclohexanone (10 mmol), phenylhydrazine hydrochlorides (10 mmol), acidic catalyst (1.0 mmol), water (15 mL).
[b] Catalyst amount: 0.5 mmol.
[c] Catalyst amount: 0.2 mmol.
[d] Reaction temperature: 80 °C.
[e] The reaction was carried out in oil bath at 100 °C.
[f] The reaction was carried out using phenylhydrazine instead of phenylhydrazine hydrochlorides.

Fig. 2. Absorption spectra of 3-nitroaniline for various acids and ILs in ethanol.

Table 2
Recycling of the catalyst system in the microwave-assisted Ficsher indole synthesis of 1,2,3,4-tetrahydrocarbazole.

Run	1	2	3	4	5	6	7	8	9	10	11	12
Time/min	15	15	15	15	15	15	15	15	15	15	15	15
Isolated yield (%)[a]	96	93	93	92	93	93	92	90	90	89	89	88
Isolated yield (%)[b]	50	25	–	–	–	–	–	–	–	–	–	–
pH[a]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
pH[b]	4	6	–	–	–	–	–	–	–	–	–	–

Reaction conditions: cyclohexanone (10 mmol), [a]Phenylhydrazine hydrochlorides (10 mmol) or [b]phenylhydrazine (10 mmol), [(HSO₃-p)₂im][CF₃SO₃] (0.5 mmol), water (15 mL).

Table 3
Microwave-assisted Fischer indoles synthesis from ketones/aldehydes with arylhydrazine hydrochlorides in the Catalyst system.[a]
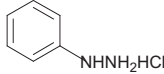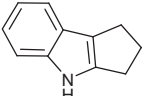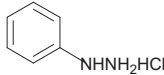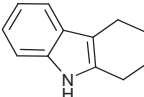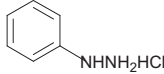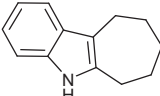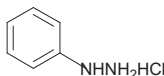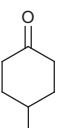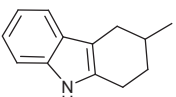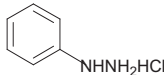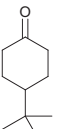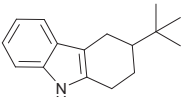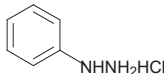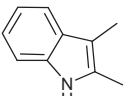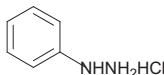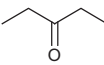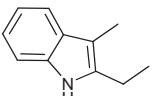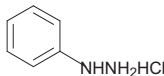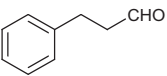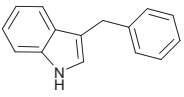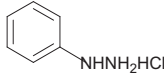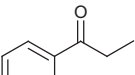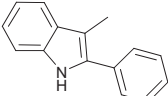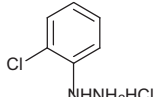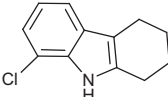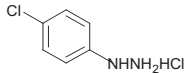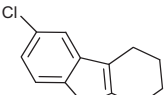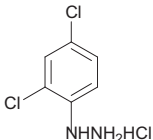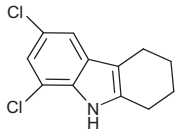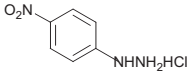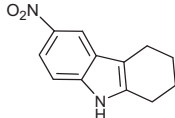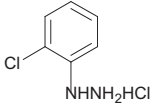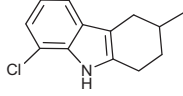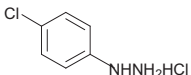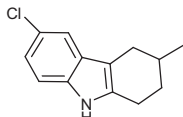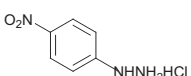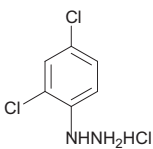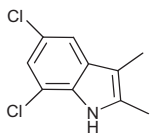
Entry	Arylhydrazines	Ketones (aldehydes)	Indoles	T (°C)	Time (min)	Isolated yield (%)
1				100	15	90
2				100	15	96
3				100	15	91
4				100	15	90
5				100	15	96
6				100	15	93
7				100	15	91
8				100	20	89
9				100	20	86
10				100	20	94
11				100	20	95

Table 3 (*Continued*)

Entry	Arylhydrazines	Ketones (aldehydes)	Indoles	T (°C)	Time (min)	Isolated yield (%)
12				100	20	90
13				100	20	87
14				100	20	90
15				100	20	89
16				100	20	88
17				100	20	86

[a] Reaction conditions: ketones/aldehydes (10 mmol), arylhydrazines (10 mmol), [(HSO$_3$-p)$_2$im][CF$_3$SO$_3$] (0.5 mmol), water (15 mL).

The acidity of the ILs with the conjugate base of [CF$_3$SO$_3$]$^-$ was stronger than that of the corresponding ILs with the conjugate base of [Cl]$^-$, [H$_2$PO$_4$]$^-$, [HSO$_4$]$^-$ and even stronger than CF$_3$SO$_3$H and H$_2$SO$_4$. The obtained acidic ILs are water-stable, nonvolatile, and immiscible in non-polar organic solvents (Scheme 2).

The one-pot Fischer indole synthesis of cyclohexanone with phenylhydrazine hydrochloride was conducted as a model reaction for the evaluation of the catalytic activity of the above Brønsted acidic ILs in water medium under microwave irradiation. To the best of our knowledge, a few reports have dealt with the application of SO$_3$H-functionalized ILs as Brønsted acid catalysts for the Fischer indole synthesis in aqueous media. Only two reports mentioned the Fischer indole synthesis using phenylhydrazine hydrochlorides as substrate [10a,b], and only two reports mentioned the Fischer indole synthesis assisted by microwave irradiation [6c,10c]. We envisioned that the aforementioned SO$_3$H-functionalized Brønsted acidic ILs are not only water stable but also miscible in water. Consequently, we expected that they could fully show all the required aspects as acid-catalysis in water. The model reaction was initially carried out under microwave irradiation at 100 °C. As shown in Table 1, CAN and p-TsOH were proven less active than the strong acids such as HCl and CF$_3$SO$_3$H (entries 1–6). In addition, the ILs exhibited a significant effect on the catalytic activity. The ILs bearing only one alkyl sulfonic acid group on the cations exhibited lower activity than the ILs bearing two alkyl sulfonic acid groups (entries 7–10 vs. entries 11–12). The activity of [Cl]-type ILs bearing two alkyl sulfonic acid groups was still inferior to that of HCl (entry 7 vs. entry 3). The activity of [H$_2$PO$_4$]-, [HSO$_4$]-, and [CF$_3$SO$_3$]-type ILs was better compared with that of

H$_3$PO$_4$, H$_2$SO$_4$, and CF$_3$SO$_3$H, respectively (entry 8 vs. entry 4; entry 9 vs. entry 5; entry 10 vs. entry 6). The product yield was changed slightly when the amount of the acid catalyst [(HSO$_3$-p)$_2$im][CF$_3$SO$_3$] was reduced from 5 mol% to 2 mol% (entry 12 vs. entry 13), and as shown in entries 14 and 15, reaction at lower temperature (80 °C vs. 100 °C, entry 14) or shorter reaction time (10 min vs. 15 min, entry 15) resulted in slightly lower yield of the product (92% and 89%), respectively. The [(HSO$_3$-p)$_2$im][CF$_3$SO$_3$]-catalyzed reaction could also be performed in an oil bath at 100 °C, leading to 80% yield of the desired product after an hour (entry 16). Furthermore, using phenylhydrazines instead of phenylhydrazine hydrochlorides afforded 50% of the yield (entry 17). Notably, [(HSO$_3$-p)$_2$im][CF$_3$SO$_3$] should be a suitable catalyst for the Fischer indole synthesis, and microwave irradiation accelerated the reaction.

Aside from the efficient and environmental benign reaction system, the simplicity of the product separation and the possibility to recycle the [(HSO$_3$-p)$_2$im][CF$_3$SO$_3$]/H$_2$O system offer significant advantag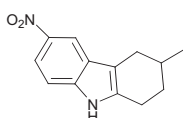es. The indole products which we prepared are insoluble in water. Hence, the products could be conveniently separated via filtration without the need of organic solvents for extraction of the product after the reaction. The remaining catalyst system could be directly reused for subsequent catalytic cycles of the aqueous reaction without the need of any treatment. After 12 times of recycle use, the accumulated ammonium chloride will be saturated in the catalyst system. After the removal of water under a vacuum, the sample was washed twice with 5 mL of 95% ethanol and filtered under suction. The filtrate was concentrated, and the recovered ILs were obtained. The recycling procedure was very

simple. The catalyst system could be reused directly without obvious decrease in the catalytic activity, pH and the product yield during 12 times of recycle use. However, under the same conditions, the use of phenylhydrazine as a substrate led to 25% yield after 2 times of recycle use, and the pH of the reaction system declined to 6.0 (Table 2) because of the liberation of ammonia during the formation of the indole compound.

Based on the above results, the generality of the reaction in the catalyst system was investigated for the synthesis of various indole products. As shown in Table 3, the catalyst system exhibited very high activities for Fischer indole synthesis. The desired indole compounds were obtained in 90% to 96% yields by the reactions of aryhydrazine hydrochlorides with cyclic ketones within 15 min at 100 °C (entries 1–5). Under the similar reaction conditions, aliphatic aldehyde and ketones as well as aryl ketone (propiophenone) gave the corresponding indoles in 86–96% yields (entries 6–9). Reactions of aryhydrazine hydrochlorides having electron-withdrawing groups completed within 20 min at 100 °C to provide the corresponding indoles in 86% to 95% yields (entries 10–17).

3. Conclusion

In this paper, an environmental benign process for one-pot microwave-assisted Fischer indole synthesis in a water medium was established using novel SO_3H-functionalized Brønsted acidic ILs bearing two alkyl sulfonic acid groups of the imidazolium cations and aryhydrazine hydrochlorides instead of aryhydrazines. Thus, $[(HSO_3-p)_2im][CF_3SO_3]$ exhibited the most efficient result for transformation in water. The results reflect that the developed methodology could offer significant improvements.

First, the entire process for the Fischer indoles was performed in water without the need of organic solvents. Aryhydrazine hydrochlorides are readily available, safe, low-toxic, and cheap substrates that are more effective than phenylhydrazines. Second, the reaction–separation–recycle process was quite convenient, and the catalytic system of $[(HSO_3-p)_2im][CF_3SO_3]/H_2O$ could be reused directly at least 12 times without a notable decrease in catalytic activity. Third, the novel catalytic system effected by a small amount of ILs (0.05 equivalent) could be successfully applied to the Fischer indole synthesis using both single-carbonyl ketones and cyclohexane-1,3-diones to afford good to excellent yields. Further investigations involving the effectiveness of the benign catalytic system for other reactions are currently underway.

4. Experimental

4.1. General remarks

NMR data were obtained on Bruker AVANCE III 500 MHz for ^{1}H at 500 MHz and for ^{13}C at 125 MHz with TMS as the internal standard. GC–MS experiments were performed on an Agilent 6890N GC system with a 5973N mass selective detector. All of the commercially available chemicals were the highest grade and used without further purification.

4.2. Representative procedure for the preparation of the Brønsted acidic ILs

Under vigorous stirring, 1,3-propane sultone (0.2 mol) was added slowly to trimethylsilylimidazole (0.1 mol), while the flask was cooled in an ice bath. After the reaction had finished, the reaction mixture was stirred for 30 min and then water was added dropwise. The reaction mixture was then dried under vacuum to remove water. The product trimethylsilyl ether compound provided the requisite precursor zwitter ion after the addition of water. Subsequently, a stoichiometric amount of H_2SO_4, HCl,

H_3PO_4, or CF_3SO_3H was added slowly to the aqueous solution of the zwitterions. The mixture was stirred for 6 h at reflux and then dried under a vacuum to obtain the final products of the desired novel SO_3H-functionalized ILs bearing two alkyl sulfonic acid groups. The products were obtained in 92–95% yields and in high purities.

$[(HSO_3-p)_2im][CF_3SO_3]$: ^{1}H NMR (500 MHz, D_2O, δ ppm): 2.14–2.19 (m, 4H), 2.76–2.79 (t, 4H, J = 7.5 Hz), 4.20–4.23 (t, 4H, J = 7.5 Hz), 7.39–7.41 (d, 2H, J = 1.5 Hz), 8.70 (s, 1H). ^{13}C NMR (125 MHz, D_2O, δ ppm): 20.9(2C), 28.1(2C), 49.0, 50.1(2C), 122.5(2C), and 135.3.

4.3. Representative procedure for the one-pot Fischer indole synthesis

Cyclohexanone (0.91 g, 10.0 mmol) was mixed with $[(HSO_3-p)_2im][CF_3SO_3]$ (0.5 mmol) in water (15 mL), and phenylhydrazine hydrochloride (1.44 g, 10.0 mmol) was added. The mixture was then stirred at 100 °C for about 15 min under microwave irradiation. Reaction progress was monitored by GC–MS. After completion, the reaction mixture was cooled to room temperature, and 1,2,3,4-tetrahydrocarbazole was obtained by filtration. The remaining mixture of $[(HSO_3-p)_2im][CF_3SO_3]/H_2O$ was reused directly. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 1.86–1.93 (m, 4H), 2.70–2.74 (m, 4H), 7.05–7.12 (m, 2H), 7.27–7.29 (d, 1H, J = 7.5 Hz), 7.45–7.47 (d, 1H, J = 7.5 Hz), 7.67 (s, 1H). (Experimental procedures, spectra and NMR data for the complexes see supporting information)

4.4. UV–vis acidity evaluation

Tested ethanol solutions were prepared from dried ethanol, 3-nitroanline and ILs, or 98% H_2SO_4, 85% H_3PO_4, 37% HCl and 99% CF_3SO_3H. All the spectra were recorded on a SHIMADZU UV-2401PC spectrophotometer at room temperature.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.09.010.

References

[1] (a) D.A. Horton, G.T. Bourne, M.L. Smythe, Chemical Reviews 103 (2003) 893–930;
(b) R.J. Sundberg, The Chemistry of Indoles, Academic Press, New York, 1970
(c) R.K. Brown, in: W.J. Houlihan (Ed.), Indoles, Wiley Interscience, New York, 1972
[2] For reviews, see:
(a) R.B. Van Order, H.G. Lindwall, Chemical Reviews 30 (1942) 69–96;
(b) G.W. Gribble, Journal of the Chemical Society, Faraday Transactions 1 (2000) 1045–1075;
(c) S. Cacchi, G. Fabrizi, Chemical Reviews 105 (2005) 2873–2920;
(d) G.R. Humphrey, J.T. Kuethe, Chemical Reviews 106 (2006) 2875–2911;
(e) K. Krüger (née Alex), A. Tillack, M. Beller, Advanced Synthesis and Catalysis 350 (2008) 2153–2167;
For selected recent examples of indole synthesis, see:
(f) S. Wurtz, S. Rakshit, J.J. Neumann, T. Droge, F. Glorius, Angewandte Chemie International Edition 47 (2008) 7230–7233;
(g) D.R. Stuart, M. Bertrand-Laperle, K.M.N. Burgess, K. Fagnou, Journal of the American Chemical Society 130 (2008) 16474–16475;
(h) Y. Ohta, H. Chiba, S. Oishi, N. Fujii, H. Ohno, Organic Letters 10 (2008) 3535–3538;
(i) N. Isono, M. Lautens, Organic Letters 11 (2009) 1329–1331;
(j) Y. Ohta, S. Oishi, N. Fujii, H. Ohno, Organic Letters 11 (2009) 1979–1982;
(k) C.H. Oh, S. Karmakar, H. Park, Y. Ahn, J.W. Kim, Journal of the American Chemical Society 132 (2010) 1792–1793;
(l) H. Shimamura, S.P. Breazzano, J. Garfunkle, F.S. Kimball, J.D. Trzupek, D.L. Boger, Journal of the American Chemical Society 132 (2010) 7776–7783;
(m) Y. Liu, B. Yao, C.-L. Deng, R.-Y. Tang, X.-G. Zhang, J.-H. Li, Organic Letters 13 (2011) 1126–1129;
(n) Z. Chen, D. Zheng, J. Wu, Organic Letters 13 (2011) 848–851.
[3] For reviews, see:
(a) B. Robinson, Chemical Reviews 63 (1963) 373–401;
(b) B. Robinson, Chemical Reviews 69 (1969) 227–250;
For selected recent examples of Fischer indole synthesis, see:
(c) H.-S. Mun, W.-H. Ham, J.-H. Jeong, Journal of Combinatorial Chemistry 7 (2005) 130–135;

(d) A.M. Schmidt, P. Eilbracht, Journal of Organic Chemistry 70 (2005) 5528–5535;
(e) P. Linnepe, A.M. Schmidt, P. Eilbracht, Organic & Biomolecular Chemistry 4 (2006) 302–313;
(f) B.P. Bondzic, A. Farwick, J. Liebich, P. Eilbracht, Organic & Biomolecular Chemistry 6 (2008) 3723–3731;
(g) H. Chen, L.S. Eberlin, M. Nefliu, R. Augusti, R.G. Cooks, Angewandte Chemie International Edition 47 (2008) 3422–3425;
(h) A.H. Benjamin, Z.-G. Zhang, J.-S. Li, P. Knochel, Angewandte Chemie International Edition 49 (2010) 9513–9516;
(i) T.P. Nitin, K. Ashok, European Journal of Organic Chemistry (2010) 6831–6839.
[4] (a) V. Hegde, P. Madhukar, J.D. Madura, R.P. Thummel, Journal of the American Chemical Society 112 (1990) 4549–4550;
(b) Y.K. Lim, C.G. Cho, Tetrahedron Letters 45 (2004) 1857–1859;
(c) E. Yasui, M. Wada, N. Takamura, Tetrahedron Letters 47 (2006) 743–746;
(d) K.G. Liu, A.J. Robichaud, J.R. Lo, J.F. Mattes, Y. Cai, Organic Letters 8 (2006) 5769–5771.
[5] (a) J.L. Rutherford, M.P. Rainka, S.L. Buchwald, Journal of the American Chemical Society 124 (2002) 15168–15169;
(b) L. Ackermann, R. Born, Tetrahedron Letters 45 (2004) 9541–9544;
(c) T.M. Lipiska, S.J. Czarnocki, Organic Letters 8 (2006) 367–370;
(d) K. Alex, A. Tillack, N. Schwarz, M. Beller, Angewandte Chemie International Edition 47 (2008) 2304–2307.
[6] (a) D. Bhattacharya, D.W. Gammon, E. van Steen, Catalysis Letters 61 (1999) 93–97;
(b) S.B. Mhaske, N.P. Argade, Tetrahedron 60 (2004) 3417–3420;
(c) A. Dhakshinamoorthy, K. Pitchumani, Applied Catalysis A-General 292 (2005) 305–311.
[7] For selected reviews on task-specific ionic liquids, see:
(a) K. Binnemans, Chemical Reviews 105 (2005) 4148–4204;
(b) C. Baudequin, D. Brégeon, J. Levillain, F. Guillen, J.-C. Plaquevent, A.-C. Gaumont, Tetrahedron: Asymmetry 16 (2005) 3921–3945;

(c) Z. Fei, T.J. Geldbach, D. Zhao, P.J. Dyson, Chemistry-A European Journal 12 (2006) 2122–2130;
(d) H. Ohno, K. Fukumoto, Accounts of Chemical Research 40 (2007) 1122–1129;
For selected recent examples of acidic ionic liquids, see:
(e) Z. Fei, D. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, Chemistry-A European Journal 10 (2004) 4886–4893;
(f) S. Li, Y. Lin, H. Xie, S. Zhang, J. Xu, Organic Letters 8 (2006) 391–394;
(g) H. Zhang, F. Xu, X. Zhou, G. Zhang, C. Wang, Green Chemistry 9 (2007) 1208–1211;
(h) D. Zhao, J. Wang, E. Zhou, Green Chemistry 9 (2007) 1219–1222;
(i) A. Fernicola, S. Panero, B. Scrosati, M. Tamada, H. Ohno, ChemPhysChem 8 (2007) 1103–1107.
[8] (a) G.L. Rebeiro, B.M. Khadikar, Synthesis 3 (2001) 370–372;
(b) R.C. Morales, V. Tambyrajah, P.R. Jenkins, D.L. Davies, A.P. Abbott, Chemical Communications (2004) 158–159;
(c) D.-Q. Xu, W.-L. Yang, S.-P. Luo, B.-T. Wang, J. Wu, Z.-Y. Xu, European Journal of Organic Chemistry 6 (2007) 1007–1012.
[9] D.-Q. Xu, J. -Wu, S.-P. Luo, J.-X. Zhang, J.-Y. Wu, X.-H. Du, Z.-Y. Xu, Green Chemistry 11 (2009) 1239–1246.
[10] (a) P. Prabhakara Varma, B.S. Sherigara, K.M. Mahadevan, V. Hulikal, Synthetic Communications 39 (2009) 158–165;
(b) S.V. Karthikeyan, S. Perumal, K.A. Shetty, P. Yogeeswari, D. Sriram, Bioorganic & Medicinal Chemistry Letters 11 (2009) 3006–3008;
(c) H.G. Kathrotiya, R.G. Patel, M.P. Patel, Journal of the Serbian Chemical Society 76 (2011) 1–22;
(d) R. Ling, M. Yoshida, P.S. Mariano, Journal of Organic Chemistry 61 (1996) 4439–4449.
[11] (a) H. Xing, T. Wang, Z. Zhou, Y. Dai, Journal of Molecular Catalysis A: Chemical 264 (2007) 53–59;
(b) Y. Wang, D. Jiang, L. Dai, Catalysis Communications 9 (2008) 2475–2480.