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An Efficient and Green Preparation of 9-Arylacridine-1,8-dione Derivatives

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ABSTRACT: *9-Arylacridine-1,8-dione derivatives were prepared in an ionic liquid medium in the presence of $CeCl_3 \cdot 7H_2O$ through an one-pot procedure. The method presented here has the advantages of environmental benignancy, good-to-excellent yields, and simple operational procedure. Moreover, the solvent and catalyst can be easily recovered and reused for several runs without obvious loss of activity.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:786–790, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20410

INTRODUCTION

It has been reported that acridine-1,8-diones can be used as laser dyes with very high-lasing efficiencies [1,2]. In addition, they have attracted many interests in view of the unique photochemical and electrochemical behavior of heterocyclic compounds. In particular, they possess bichromophoric groups, which enable them to act as both electron donors and acceptors in the excited state [3,4] and, thus, have been used in the photoinitiated polymerization of acrylates and methacrylates [5]. Moreover, acridinediones have structural similarity to those of 1,4-dihydropyridines (1,4-DHPs), which are versatile intermediates in the synthesis of numerous pharmaceuticals including those for the treatment of cardiovascular diseases [6] and congestive heart failure [7]. Classical methods for the synthesis of 1,4-dihydropyridines involve the condensation of an aldehyde with ethyl acetoacetate and ammonia either in acetic acid or in ethanol [8]. As for the preparation of acridine-1,8-diones, similar methods have been employed and they are usually carried out in organic solvents such as methanol or acetic acid through a two-step procedure [9]. These procedures usually require tedious works to isolate the intermediate products and necessitate the use of classical organic solvents, which are inevitably hazardous to some extent to the environment. Recently, it has been reported that acridine-1,8-diones can also be obtained under microwave irradiation conditions [10]. Although microwave heating provides a time-efficient methodology, more works are definitely still needed to develop more practical and more environmentally benign methods.

Recently, room temperature ionic liquids have shown great promise as green reaction media in the realm of synthetic organic chemistry [11]. Of particular interest are air and moisture stable imidazolium ionic liquids, which have been used as solvents for a large variety of organic reactions due to their favorable properties, such as nonvolatile, nonexplosive, recyclable, easy to handle, and thermally robust [12]. In many cases, the products are weakly soluble in the ionic phase and thus can be easily separated

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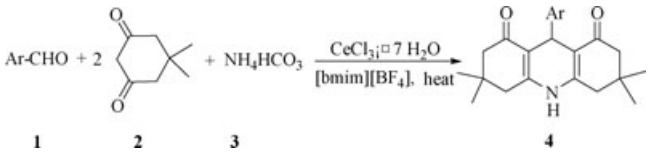


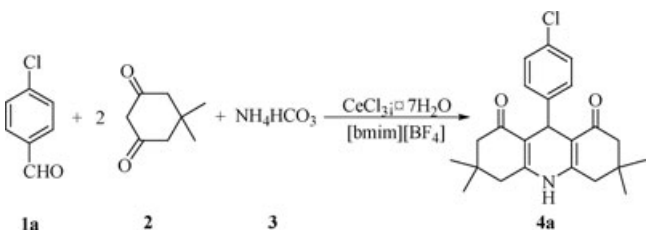
SCHEME 1

by filtration or simple extraction with ether [13]. Therefore, many problems arisen from the use of volatile organic solvents can be avoided. On the other hand, $CeCl_3 \cdot 7H_2O$ has recently emerged as an attractive candidate as a moderate Lewis acid [14] due to its relative nontoxicity, water stability, ready availability at a low cost [15], and high selectivity as a promoter. As part of our program aimed at developing environmental friendly methodologies in organic synthesis, herein, we would like to report an one-pot reaction of aldehyde (**1**), 5,5-dimethyl-1,3-cyclohexandione (**2**), and ammonium bicarbonate (**3**) for the preparation of acridine-1,8-dione (**4**) promoted by a catalytic amount of cerium(III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$) by using the ionic liquid, 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF_4]) as solvent (Scheme 1).

RESULTS AND DISCUSSION

We started our work by examining the possibility of an one-pot reaction involving *p*-chlorobenzaldehyde (**1a**), **2**, and **3** to afford 3,3,6,6-tetramethyl-9-(4-chlorophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8 (2H,7H)-dione (**4a**) in ([bmim][BF_4]) in the presence or absence of $CeCl_3 \cdot 7H_2O$ (Scheme 2).

It turned out that after the mixture of **1a, 2**, and **3** in 1.0 mL [bmim][BF_4] being stirred for 16 h at 80°C, **4a** could be obtained but with a rather low yield (41%) (Table 1, entry 1). Then, 0.15 mmol $CeCl_3 \cdot 7H_2O$ was introduced in the above reaction. After being stirred at 80°C for 10 h, it afforded **4a** with a much higher yield (68%), demonstrating obvious catalytic activity of $CeCl_3 \cdot 7H_2O$ for this reaction



SCHEME 2

(Table 1, entry 2). To further improve the reaction, a new operating procedure was then attempted by first treating **2** (0.5 mmol) and **3** (1.2 mmol)* in 1.0 mL ionic liquid together with 0.15 mmol $CeCl_3 \cdot 7H_2O$. After the mixture being stirred for 3 h at 55°C, **2** was completely consumed and the corresponding enamine intermediate was formed (monitored by TLC). Without isolating of this intermediate, **1a** (0.5 mmol) and another 0.5 mmol of **2** were added to the reaction mixture. After being stirred at 100°C for another 3 h, it gave **4a** with a very good yield (91%; Table 1, entry 3). Furthermore, the optimal amount of $CeCl_3 \cdot 7H_2O$ for this procedure was also investigated (Table 1, entry 4–6). It soon turned out that as less as 0.05 mmol $CeCl_3 \cdot 7H_2O$ was enough to give a very good result as 0.15 mmol $CeCl_3 \cdot 7H_2O$ did (Table 1, entry 5).

With the above result in hand, we then extended this procedure to a variety of aromatic aldehydes. It turned out that all the substrates investigated underwent the reactions smoothly and gave the corresponding products in good to excellent yields. The results are summarized in Table 2. It should also be noted here that all of the reactions were carried out smoothly under mild conditions, and there was no need to exclude moisture or oxygen from the reaction system.

With efforts for a greener chemistry, the possibility of the recovery and reutilization of the catalyst and solvent was then studied. At the completion of the reaction, the product was in fact in a solid state so it could be simply collected by suction. The filtrate containing [bmim][BF_4] together with the immobilized Ce(III) was then dried at 100°C for several hours until its mass was independent of drying time. Investigations by using **1a** as a model substrate showed that successive reuse of the recovered ionic liquid and catalyst in the same reaction gave the product with a yield of 92%, even higher than that of the first round (Table 3, entry 2). It also has been observed that even in the fifth round, the corresponding product still could be obtained with fairly good yield by using the ionic liquid and the catalyst recovered from the fourth round (Table 3, entry 5).

Furthermore, it has been reported that ionic liquids not only are able to be used as a green recyclable alternative to classical organic solvents, but also has the advantages of actually accelerating

* Because the ammonium bicarbonate was prone to decompose and part of the ammonia would run out, the reaction would carried out more efficiently if the addition of **3** was divided into 3 parts (i.e., first added 0.5 mmol, then another 0.5 mmol, at last added 0.2 mmol).

TABLE 1 Reaction Condition Screening for the Preparation of the Compound of **4a**

Entry	*Amount of $CeCl_3 \cdot 7H_2O$ (mmol)*	*Reaction Time (h)*	*Reaction Temperature (°C)*	*Isolated Yields (%)*
1	0.00	16	80	41
2	0.15	10	80	68
3	0.15	3,3	55,100	91
4	0.10	3,3	55,100	91
5	0.05	3,3	55,100	89
6	0.025	4,4	55,100	80

TABLE 2 Preparation of **4a–4j** Promoted by $CeCl_3 \cdot 7H_2O$ in [bmim][BF_4]

Entry	*Ar*	*Products*[a]	*Yield*[b] *(%)*
1	*p*-ClC_6H_4	**4a**	89
2	C_6H_5	**4b**	88
3	*p*-$CH_3C_6H_4$	**4c**	87
4	*p*-$NO_2C_6H_4$	**4d**	93
5	*m*-$NO_2C_6H_4$	**4e**	88
6	*o*-$NO_2C_6H_4$	**4f**	82
7	*p*-BrC_6H_4	**4g**	95
8	*o*-BrC_6H_4	**4h**	85
9	*o*-ClC_6H_4	**4i**	86
10	*p*-OH,*m*-$OCH_3C_6H_4$	**4j**	94

[a]All the products were characterized by their ^1H NMR and IR spectra and compared with authentic samples.
[b]Isolated yields.

the reaction process and increasing the yields compared with classical solvents [16]. To clarify whether [bmim][BF_4] has such advantages in this reaction, the above procedure was also tried in some traditional organic solvents, such as anhydrous ethanol, THF, CH_2Cl_2, and CH_3CN. By using **1a** as the model substrate again, investigation showed that through similar operational procedure under similar reaction conditions, reactions carried out in these organic solvents only gave the corresponding product in rather disappointingly low yields compared with the case when [bmim][BF_4] was used (Table 4). Moreover, the separation process was much more tedious in which several runs of extraction of the product and removal of the solvents were necessitated.

TABLE 3 Reusability of [bmim][BF_4] and the Catalyst for the Preparation of **4b**

Round	*Ionic Liquid Recovered (%)*	*Yield (%)*[a,b]
1	98	89
2	99	92
3	98	90
4	99	88
5	98	89

[a]0.05 mmol $CeCl_3 \cdot 7H_2O$ was used for 0.5 mmol **1a** and 1.0 mmol **2**.
[b]Isolated yields.

TABLE 4 The Preparation of **4a** in Different Solvents

Entry	*Solvent*	*Reaction Time (h)*	*Reaction Temperature (°C)*	*Yield (%)*[a,b]
1	Ethanol	3,3	55, reflux	48
2	THF	3,3	55, reflux	37
3	CH_2Cl_2	6	Reflux	42
4	CH_3CN	3,3	55, reflux	54
5	[bmim][BF_4]	3,3	55, 100	89

[a]0.05 mmol $CeCl_3 \cdot 7H_2O$ was used for 0.5 mmol **1a** and 1.0 mmol **2**.
[b]Isolated yields.

In summary, this report discloses a novel and simple method for the synthesis of 9-arylacridine-1,8-dione derivatives. Advantages of this $CeCl_3 \cdot 7H_2O$ catalyzed one-pot procedure include simple operational procedure, high efficiency, mild reaction condition together with an environmental friendly nature. Furthermore, the solvent and catalyst can be easily recovered and reused. All of these are expected to offer a green and efficient alternative for the synthesis of 9-arylacridine-1,8-diones.

EXPERIMENTAL

Melting points were measured by a Kofler micromelting point apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrometer in KBr with absorption in cm^{-1}. ^1H NMR spectra were determined on a Bruker AC 400 spectrometer as $CDCl_3$ solutions. Chemical shifts (δ) are expressed in ppm downfield from the internal standard tetramethylsilane (TMS), and coupling constants J are given in Hz. ^{13}C NMR spectra were determined on a Bruker AC 300 spectrometer as $CDCl_3$ solutions and using TMS as the internal standard. Mass spectra were recorded on a HP5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument.

The ionic liquid [bmim][BF_4] was prepared and purified according to the literature procedure [17]. Other reagents were of reagent grade and were used without further purification.

General Procedure for the Preparation of 9-Arylacridine-1,8-dione Derivatives

First, 5,5-dimethyl-1,3-cyclohexanedione (**2**, 0.5 mmol) and ammonium bicarbonate (**3**, 1.2 mmol) were added to a 10-mL round bottom flask containing 1.0 mL [bmim][BF_4] and 0.05 mmol $CeCl_3 \cdot 7H_2O$. Then, the mixture was stirred at 55°C for about 3 h to complete the reaction (monitored by TLC). Without isolating the intermediate product, aromatic aldehyde (**1**, 0.5 mmol) and another 0.5 mmol of **2** were added to the reaction mixture and let it being stirred for about another 3 h at the temperature of 100°C. Upon completion, the reaction mixture was added with water and the solid was collected by suction and rinsed with water and ether. Then, the solid obtained was further purified by recrystallization from 95% ethanol to give the pure products **4**. All the products were fully characterized by ^{1}H NMR, IR, and elemental analysis. The aqueous solution of ionic liquid together with the catalyst was concentrated under the reduced pressure and dried at 100°C to recover the ionic liquid and catalyst for the subsequent use.

*3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4a**).* 298–300°C (lit. [10c] 296–298°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.94 (s, 6H, 2×CH_3), 1.06 (s, 6H, 2×CH_3), 2.12–2.31 (m, 8H, 4×CH_2), 5.05 (s, 1H, CH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 7.27 (d, J = 8.0 Hz, 2H, ArH), 7.73 (s, 1H, NH); IR (KBr): 3433 (NH), 1650 (C=O), 1610 (N–C=C) cm^{-1}.

*3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4b**).* 258–260°C (lit. [9] 250–252°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.97 (s, 6H, 2×CH_3), 1.08 (s, 6H, 2×CH_3), 2.14–2.35 (m, 8H, 4×CH_2), 5.11 (s, 1H, CH), 7.08 (t, J = 8.0 Hz, 1H, ArH), 7.20 (t, J = 8.0 Hz, 2H, ArH), 7.35 (d, J = 8.0 Hz, 2H, ArH), 7.55 (s, 1H, NH); IR (KBr): 3439 (NH), 1640 (C=O), 1606 (N–C=C) cm^{-1}.

*3,3,6,6-Tetramethyl-9-(4-methylphenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4c**).* 318–320°C (lit. [18] > 300°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.94 (s, 6H, 2×CH_3), 1.04 (s, 6H, 2×CH_3), 2.11–2.29 (m, 11H, 4×CH_2, CH_3), 5.04 (s, 1H, CH), 6.97 (d, J = 8.0 Hz, 2H, ArH), 7.21 (d, J = 8.0 Hz, 2H, ArH), 7.99 (s, 1H, NH); IR (KBr): 3443 (NH), 1651 (C=O), 1607 (N–C=C) cm^{-1}.

*3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4d**).* 288–289°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.95 (s, 6H, 2×CH_3), 1.09 (s, 6H, 2×CH_3), 2.08–2.44 (m, 8H, 4×CH_2), 5.15 (s, 1H, CH), 6.14 (s, 1H, NH), 7.50 (d, J = 8.0 Hz, 2H, ArH), 8.06 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 27.13, 29.41, 32.72, 34.40, 41.25, 50.53, 112.81, 123.37, 129.02, 145.83, 147.84, 153.68, 195.07; IR (KBr): 3444 (NH), 1643 (C=O), 1604 (N–C=C) cm^{-1}; MS (70 eV) m/z: 394 (M^+); Anal. Calcd. for $C_{23}H_{26}N_2O_4$: C, 70.03; H, 6.64; N, 7.10. Found: C, 70.20; H, 6.56; N, 7.00.

*3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4e**).* 294–296°C (lit. [10a] 285–286°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.97 (s, 6H, 2×CH_3), 1.09 (s, 6H, 2×CH_3), 2.13–2.43 (m, 8H, 4×CH_2), 5.16 (s, 1H, CH), 6.14 (s, 1H, NH), 7.37 (t, J = 8.0 Hz, 1H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 7.94 (d, J = 8.0 Hz, 1H, ArH), 8.02 (s, 1H, ArH); IR (KBr): 3444 (NH), 1648 (C=O), 1609 (N–C=C) cm^{-1}.

*3,3,6,6-Tetramethyl-9-(2-nitrophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4f**).* 293–295°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.97 (s, 6H, 2×CH_3), 1.07 (s, 6H, 2×CH_3), 2.10–2.31 (m, 8H, 4×CH_2), 5.72 (s, 1H, CH), 6.48 (s, 1H, NH), 7.19 (t, J = 8.0 Hz, 1H, ArH), 7.41 (t, J = 8.0 Hz, 1H, ArH), 7.53 (d, J = 8.0 Hz, 1H, ArH), 7.65 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 27.56, 28.99, 31.83, 32.51, 41.22, 50.61, 112.67, 124.16, 126.72, 131.68, 131.93, 135.32, 140.07, 148.35, 195.17; IR (KBr): 3439 (NH), 1635 (C=O), 1595 (N–C=C) cm^{-1}; MS (70 eV) m/z: 394 (M^+); Anal. Calcd. for $C_{23}H_{26}N_2O_4$: C, 70.03; H, 6.64; N, 7.10. Found: C, 70.18; H, 6.58; N, 7.05.

*3,3,6,6-Tetramethyl-9-(4-bromophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4g**).* 312–315°C. ^{1}H NMR($CDCl_3$, 400 MHz) δ: 0.95 (s, 6H, 2×CH_3), 1.07 (s, 6H, 2×CH_3), 2.12–2.35 (m, 8H, 4×CH_2), 5.03 (s, 1H, CH), 6.95 (s, 1H, NH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR($CDCl_3$, 300 MHz) δ: 27.13, 29.49, 32.66, 33.42, 41.01, 50.70, 113.18, 119.77, 129.88, 131.00, 145.51, 148.11, 195.47; IR (KBr): 3444 (NH), 1647 (C=O), 1610 (N–C=C) cm^{-1}; MS (70 eV) m/z: 429 ($M^+ + 2$), 427 (M^+); Anal. Calcd. for $C_{23}H_{26}BrNO_2$: C, 64.49; H, 6.12; N, 3.27. Found: C, 64.52; H, 6.28; N, 3.05.

*3,3,6,6-Tetramethyl-9-(2-bromophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (**4h**).* >300°C(decompose). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.99 (s, 6H, 2×CH_3), 1.07 (s, 6H, 2×CH_3), 2.10–2.36 (m, 8H, 4×CH_2), 5.31 (s, 1H, CH), 6.23 (s, 1H, NH), 6.92 (t, J = 8.0 Hz, 1H, ArH), 7.15 (t, J = 8.0 Hz, 1H,

ArH), 7.42 (d, $J = 8.0$ Hz, 2H, ArH);^{13}C NMR($CDCl_3$, 300 MHz) δ: 27.46, 29.33, 32.48, 36.27, 41.36, 50.66, 112.89, 123.31, 126.67, 127.46, 132.83, 133.31, 144.34, 147.65, 195.17; IR (KBr): 3433 (NH), 1650 (C=O), 1612 (N—C=C) cm^{-1}; MS (70 eV) *m/z*: 429 ($M^+ + 2$), 427 (M^+); Anal. Calcd for $C_{23}H_{26}BrNO_2$: C, 64.51; H, 6.12; N, 3.27. Found: C, 64.49; H, 6.22; N, 3.03.

*3,3,6,6-Tetramethyl-9-(2-chlorophenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (***4i***).* 220–222°C (lit. [10d] 221–223°C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.98 (s, 6H, 2×CH_3), 1.07 (s, 6H, 2×CH_3), 2.10–2.38 (m, 8H, 4×CH_2), 5.30 (s, 1H, CH), 6.36 (s, 1H, NH), 7.01 (t, $J = 8.0$ Hz, 1H, ArH), 7.12 (t, $J = 8.0$ Hz, 1H, ArH), 7.20 (d, $J = 8.0$ Hz, 1H, ArH), 7.50 (d, $J = 8.0$ Hz, 1H, ArH); IR (KBr): 3436 (NH), 1637 (C=O), 1609 (N—C=C) cm^{-1}.

*3,3,6,6-Tetramethyl-9-(4-hydroxy,3-methoxyphenyl)-3,4,5,6,9,10-hexahydroacridine-1,8(2H,7H)-dione (***4j***).* 294–295°C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.98 (s, 6H, 2×CH_3), 1.08 (s, 6H, 2×CH_3), 2.19–2.39 (m, 8H, 4×CH_2), 3.87 (s, 3H, OCH_3), 4.98 (s, 1H, CH), 5.38 (s, 1H, NH), 5.73 (s, 1H, OH), 6.62 (d, $J = 8.0$ Hz, 1H, ArH), 6.69 (d, $J = 8.0$ Hz, 1H, ArH), 7.05 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 27.21, 29.48, 32.71, 33.12, 41.47, 50.73, 55.90, 112.06, 113.76, 114.20, 119.73, 125.07, 138.80, 145.99, 146.55, 195.20; IR (KBr): 3423 (NH), 1660 (C=O), 1625 (N—C=C) cm^{-1}; MS (70 eV) *m/z*: 395 (M^+); Anal. Calcd for $C_{24}H_{29}NO_4$: C, 72.89; H, 7.39; N, 3.54. Found: C, 72.78; H, 7.48; N, 3.50.

REFERENCES

[1] Prabahar, K. J.; Ramakrishnan, V. T.; Sastikumar, D.; Selladurai, S.; Masilamani, V. Indian J Pure Appl Phys 1991, 29, 382–384.

[2] Shanmugasundaram, P.; Murugan, P.; Ramakrishnan, V. T.; Srividya, N.; Ramamurthy, P. Heteroat Chem 1996, 7, 17–22.

[3] Timpe, H. J.; Ulrich, S.; Ali, S. J Photochem Photobiol, A Chem 1991, 61, 77–89.

[4] Timpe, H. J.; Ulrich, S.; Fouassier, J. P. J Photochem Photobiol 1993, 73, 139–150.

[5] Timpe, H. J.; Ulrich, S.; Decker, C.; Fouassier, J. P. Macromolecules 1993, 26, 4560–4566.

[6] Janis, R. A.; Silver, P. J.; Triggle, D. J. Adv Drug Res 1987, 16, 309.

[7] Vo, D.; Matowe, W. C.; Ramesh, M.; Iqbal, N.; Wolowyk, M. W.; Howlett, S. E.; Knaus, E. E. J Med Chem 1995, 38, 2851–2859.

[8] Loev, B.; Snader, K. M. J Org Chem 1965, 30, 1914–1916.

[9] Srividya, N.; Ramamurthy, P.; Shanmugasundaram, P.; Ramakrishnan, V. T. J Org Chem 1996, 61, 5083–5089.

[10] (a) Suarez, M.; Loupy, A.; Salfran, E.; Moran, L.; Rolando, E. Heterocycles 1999, 51, 21–27; (b) Tu, S.; Miao, C.; Gao,Y.; Fang, F.; Zhuang, Q.; Feng, Y.; Shi, D. Synlett 2004, 2, 255–258; (c) Tu, S.; Gao,Y.; Miao, C.; Li, T.; Zhang, X.; Zhu, S.; Fang, F.; Shi, D. Synth Commun 2004, 34, 1289–1294; (d) Tu, S.; Lu, Z.; Shi, D.; Yao, C.; Gao, Y.; Guo, C. Synth Commun 2002, 32, 2181–2185.

[11] Dupont, J.; De Souza, R. F.; Suarez, P. A. Z. Chem Rev 2002, 102, 3667–3691.

[12] (a) Welton, T. Chem Rev 1999, 99, 2071–2083; (b) Wasserscheid, P.; Keim, W. Angew Chem, Int Ed 2000, 39, 3773–3789; (c) Earle, M. J.; Seddon, K. R. Pure Appl Chem 2000, 72, 1391–1398.

[13] (a) Sheldon, R. Chem Commun 2001, 2399–2407; (b) Le Boulaire,V.; Gree, R. Chem Commun 2000, 2195–2196.

[14] (a) Bartoli, G.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E.; Sambri, L. Synthesis 2004, 6, 895–900; (b) Bartoli, G.; Bosco, M.; Giuliani, A.; Marcantoni, E.; Palmieri, A.; Petrini, M.; Sambri, L. J Org Chem 2004, 69, 1290–1297; (c) Bose, D. S.; Fatima, L.; Mereyala, H. B. J Org Chem 2003, 68, 587–590; (d) Ankala, S. V.; Fenteany, G. Tetrahedron Lett 2002, 43, 4729–4732; (e) Mase, N.; Nishi, T.; Hiyoshi, M.; Ichihara, K.; Bessho, J.; Yoda, H.; Takabe, K. J Chem Soc, Perkin Trans 1 2002, (6), 707–709.

[15] Imamoto, T. Lanthanides in Organic Synthesis; Academic Press: New York, 1994.

[16] Xie, Y. Y.; Chen, Z. C.; Zheng, Q. G. Synthesis 2002, 1505–1508.

[17] Holbrey, J. D.; Seddon, K. R. J Chem Soc, Dalton Trans 1999, 2133–2139.

[18] Wang, X. S.; Shi, D. Q.; Zhang, Y. F.; Wang, S. H.; Tu, S. J. Chin J Org Chem 2004, 24, 430–432.