The Combination of $TsNH_2$ and NCS as Nitrogen and Chlorine Sources for Direct Diamination of Enones

Cody Timmons,[a] Dianjun Chen,[a] Xin Xu,[a] and Guigen Li*[a]

Dedicated to Professor Henry Shine on the occasion of his 80th birthday

Keywords: Aminations / Olefins / Nitrogen heterocycles / Cycloadditions

The regio-, stereo-, and chemoselective diamination of enones has been achieved without the observation of any haloamines. The reaction employs the readily available inexpensive combination of NCS and $TsNH_2$ as an electrophilic nitrogen source, and three nitriles as nucleophilic nitrogen sources. A novel mechanism involving the formation of aziridinium intermediates from the reaction of TsNHCl with olefins and a new [2+3] cyclic addition for aziridinim ring opening has been proposed for the electrophilic diamination of olefins.

Introduction

The development of new regio- and stereoselective routes to vicinal diamine compounds has proven to be a challenging topic in organic synthesis.[1−5] These compounds are of great importance owing to their many potential applications in the medical and pharmaceutical fields.[1,2] To date, the majority of the syntheses of these important compounds centered around the use of transition metal promoters.[6] Recent work in our lab has led to several methods for the preparation of 1-*p*-tosyl-3-dichloromethyl-4,5-imidazoline[7,8] and 1-*p*-tosyl-3-trichloromethyl-4,5-imidazoline[9] compounds. These can readily be hydrolyzed by 6 N HCl to yield the corresponding protected vicinal diamine products (Scheme 1). In each case, *N*,*N*-dichloro-*p*-toluenesulfonamide ($TsNCl_2$) and MeCN were used as the electrophilic and nucleophilic nitrogen sources, respectively (Scheme 1, conditions A and B). We also discovered that α,β-unsaturated ketones react with $TsNCl_2$ and MeCN in the absence of a catalyst but with prolonged time to afford the dichlorinated imidazoline derivatives in acceptable yields.[8c]

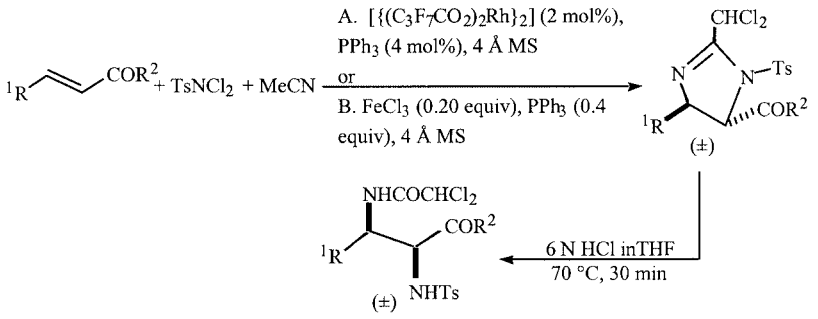
Very recently, Sudalai and co-workers developed an aminobromination methodology in which $TsNH_2$ and NBS served as the amine and bromine sources in the reaction with olefins.[10] Intrigued by their results, we sought to explore an analogous aminochlorination procedure in which NCS replaced NBS. To our surprise, we found that when MeCN was used as a solvent in the absence of any metal catalyst, aminohalogenation did not occur but the diamination product was formed. This new system has the advantage that all starting materials are readily available, whereas in the previous systems $TsNCl_2$ had to be prepared independently and used relatively quickly before it decomposed. Thus, this new system is truly a very convenient and one-pot diamination process. In this communication, we report the preliminary results of this new system (Scheme 2 and Table 1). Also, two previously unexplored nitriles, benzonitrile and isobutyronitrile, were successfully employed as nucleophilic nitrogen sources and the resulting non-halogenated products were obtained in promising yields (Table 2).

Results and Discussion

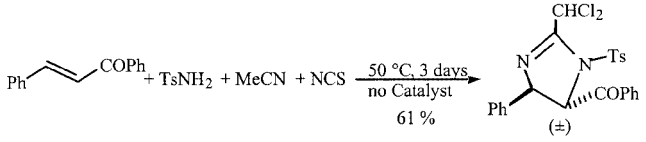
The regio and stereochemistry resulting from this $TsNH_2$/NCS-based diamination with no metal catalyst suggests that the previous mechanism hypothesis should be further modified (Scheme 3). The first step of this reaction could be the formation of *N*-monochloro-*p*-toluenesulfonamide (*p*TsNHCl) which reacts with olefin to form the *N*-(*p*-tosyl)-aziridinium intermediate **A**. To the best of our knowledge, this is the first time that aziridinium intermediates have been found to be generated by the reaction of TsNHCl with alkenes. This step is similar to that of a previous diamination process where an *N*-chloro*N*-(*p*-tosyl)aziridinium species was formed as the key intermediate.[11,12] The next step, aziridinium ring opening, could proceed through a [2+3] cyclic addition reaction between acetonitrile and *N*-(*p*-tosyl)aziridinium intermediate **A** to form 1-*N*-(*p*-tosyl)-imidazolinium **B** directly. This step controls both regio and syn stereoselectivity. After intermediate **B** is deprotonated, **C** is generated followed by chlorination by NCS to give rise

[a] Department of Chemistry and Biochemistry, Texas Tech University,
Lubbock, TX 79409-1061, USA
E-mail: Guigen.Li@ttu.edu

  DOI: 10.1002/ejoc.200300326

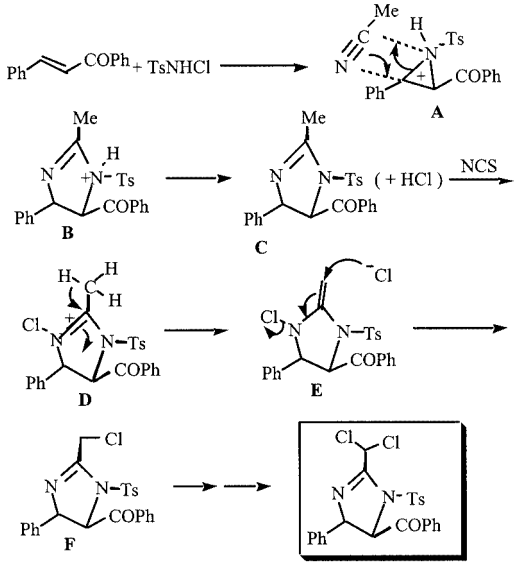


Scheme 1



Scheme 2

to **D**. Deprotonation of the 2-methyl group of **D** gives methylene scaffold **E**, which enables the second S_N2'-type displacement to afford 2-chloromethyl-4-phenyl-5-phenylcarbonyl-1-(*p*-tosyl)imidazoline (**F**), which is then converted into the final imidazoline product through further similar steps from **C** to **F**.



Scheme 3

It should be noted that this aziridinium-based mechanism can account for the regio- and stereoselectivity of the previous catalyzed aminochlorination processes.[11,12] In those systems, the S_N2 opening by chloride anion is responsible for the high anti stereoselectivity. The regioselectivity is controlled by the fact that the β-position of the aziridinium intermediate has more positive charge than the α-position because of the stabilization effect from the phenyl ring.

Similar to our previous diamination and aminohalogenation reactions, it was very convenient to carry out the present diamination simply by mixing the reactants, olefin, $TsNH_2$, NCS, and 4-Å molecular sieves in freshly distilled acetonitrile. Since there are no sensitive catalysts involved, the reaction can be performed without special protection from inert gases. The capped reaction mixture was kept stirred at 50 °C for the indicated period for each substrate as shown in Tables 1 and 2 until completion was achieved, as monitored by crude NMR analysis or TLC. Upon completion, the major side product, succinimide derived from NCS, could be readily filtered off before further purification of the diamine product.

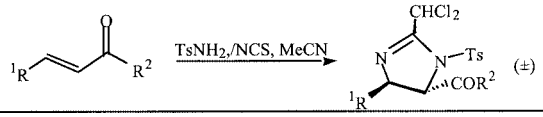
At the initial stage, chalcone was chosen as the substrate for reaction optimization. It was found that at 50 °C stoichiometric amounts of $TsNH_2$ (one equivalent) and NCS (two equivalents) afforded the product in limited yield (ca. 35−40%). Doubling the reactant quantities, i.e. two equivalents of $TsNH_2$ and four equivalents of NCS, increased the yield to around 50%. However, at 50 °C a significant amount of starting material remained even after three days. It was found, however, that addition of a further two equivalents of NCS after the reaction had proceeded for 24 h solved this problem. Furthermore, although the reaction did occur at room temperature, it proceeded very slowly. Increasing the temperature to 50 °C allowed the reaction to proceed to completion within three days. Table 1 illustrates the diamination results using acetonitrile as the co-nitrogen source.

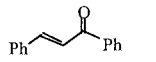
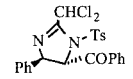
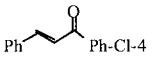
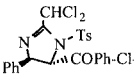
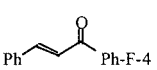
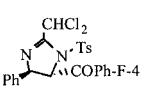
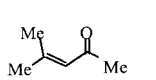
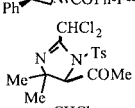
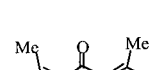
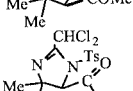
As can be seen from Table 1, terminal disubstituted ketones reacted faster and gave higher yields. In no case did cinnamate esters react to any appreciable extent, which is different from previous systems. As far as chalcone derivatives are concerned, all work well except for those with strong electron-withdrawing substituents (e.g. 3- and 4-nitrochalcone).

The use of 4 Å molecular sieves proved essential in that yields were reduced to almost one half when they were not employed. The role of the molecular sieves during the reaction mechanism is not clear at this stage. One of their possible roles could be to absorb the hydrogen chloride which is released during the reaction process.

After acetonitrile was successfully utilized for this direct diamination, two other nitriles, benzonitrile (PhCN) and

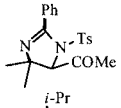
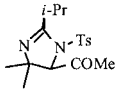
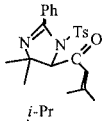
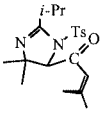
Table 1. Results of TsNH2/NCS-based diamination of α,β-unsaturated ketones



entry	substrates	product (±)		stereoselectivty[a]	time (h)	yield (%) [b]
1			**1**	>95	72	61
2			**2**	>95	72	62
3			**3**	>95	60	67
4			**4**	N/A	48	78
5			**5**	N/A	48	70

[a] Estimated by crude ^{1}H NMR determination. > 95% means no minor isomer was detected. No regio minor isomers were detected for **1**−**3**. [b] Yields after purification via column chromatography.

Table 2. Diamination using *i*PrCN and PhCN as the nitrogen sources

entry	R^1	R^2	product		time (h)	yield (%) [a]
1	Me—	Ph—		**6**	60	74
2	Me—	*i*-Pr—		**7**	60	63
3		Ph—		**8**	60	61
4		*i*-Pr—		**9**	60	74

[a] The yields after purification via column chromatography.

isobutyronitrile (*i*PrCN) were also used as nucleophilic nitrogen sources (Table 2). When these two new nitrogen sources were used as solvents in lieu of MeCN, the resulting imidazoline adducts contained no chlorine atoms. This observation indicates that S_N2'-type displacement is inhibited when using isobutyronitrile as the solvent. The steric effect of the two methyl groups of this nitrogen source could be responsible for the inhibition. Importantly, the above observation can support the present ionic mechanism instead of a radical one for the formation of carbon−chlorine bonds of the 2-methylene group of the final imidazoline product. Two substrates, phorone and mesityl oxide, were explored with these alternative nitrogen sources. As summarized in Table 2, satisfactory yields were achieved in all these cases.

The use of NBS to replace NCS as the halogen source for this diamination reaction has not yet been successful. It

seems more difficult to generate the aziridinium intermediate by the reaction between *N*-bromo-*p*-toluenesulfonamide and electron-deficient olefins. A mechanism study by the direct determination of various intermediates will be carried out in our laboratories.

Conclusion

A new method has been developed for the synthesis of imidazoline derivatives using readily available inexpensive starting materials, NCS and $TsNH_2$, under more convenient conditions. This method eliminates the need to prepare and store the relatively unstable $TsNCl_2$. Benzonitrile and isobutyronitrile were also successfully employed as nucleophilic nitrogen sources to produce non-halogenated imidazoline derivatives. This work demonstrates the first example of aziridinium intermediate formation from the reaction of TsNHCl with olefins.

Experimental Section

General Procedure: All reactions were conducted without inert gas protection. Acetonitrile was dried and freshly distilled from calcium hydride under a nitrogen atmosphere. All other chemicals were purchased commercially and used without further purification, and their stoichiometries were calculated based on the reported purities from the manufacturers. Flash chromatography was performed on silica gel 60 (230−400 mesh). ^{1}H NMR spectroscopy (500 MHz) and ^{13}C NMR spectroscopy (125 MHz) were acquired in deuterated chloroform ($CDCl_3$). High-resolution mass spectral analysis was conducted by the mass spectrometry laboratory of the Scripps Research Institute. Melting points are reported uncorrected. Products **1**, **2**, **4**, and **5** can be identified based on comparison to known compounds.

General Procedure for Direct Diamination: Olefin (1.0 mmol), 4-Å molecular sieves (0.50 g), $TsNH_2$ (342 mg, 2 mmol), NCS (534 mg, 4 mmol), and freshly distilled acetonitrile (6 mL) were added to a dry vial. The vial was capped and the contents stirred at 50 °C for 24 h, when an additional portion of NCS (267 mg, 2 mmol) was introduced. Stirring was continued at 50 °C until the reaction was complete, as monitored by crude NMR analysis or TLC, when the solid residue was filtered off and washed with EtOAc (3 × 15 mL). The resulting solution was condensed under reduced pressure and purified via flash chromatography (EtOAc/hexane, 1:4) to afford the pure product.

1: Isolated as a white solid (299 mg, 61% yield). M.p. 130−131 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 1698 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80−7.74 (m, 4 H), 7.64−7.61 (m, 1 H), 7.49−7.44 (m, 2 H), 7.32−7.23 (m, 6 H), 6.90 (dd, *J* = 1.40, 8.02 Hz, 2 H), 5.56 (d, *J* = 4.86 Hz, 1 H), 5.01 (d, *J* = 4.86 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.3, 156.7, 145.7, 138.7, 134.4, 134.3, 133.5, 130.1, 129.0(2), 128.8, 128.7, 126.6, 72.3, 71.9, 61.4, 21.7 ppm.

2: Isolated as a white solid (326 mg, 62% yield). M.p. 96−98 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 1869 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.5 Hz, 2 H), 7.69 (d, *J* = 8.5 Hz, 2 H), 7.44 (d, *J* = 8.99 Hz, 2 H), 7.33−7.26 (m, 5 H), 7.21 (s, 1 H), 6.89 (d, *J* = 8.50 Hz, 2 H), 5.48 (d, *J* = 5.00 Hz, 1 H), 5.00 (d, *J* = 5.00 Hz, 1 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.4, 156.7, 145.9, 141.0, 138.5, 134.3, 131.8, 132.0, 132.1, 129.4, 129.1, 128.8, 127.9, 126.5, 72.3, 72.0, 61.4, 21.7 ppm.

3: Isolated as a white solid (336 mg, 67%). M.p. 119−121 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 1698(C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80−7.77 (m, 3 H), 7.32 (d, *J* = 7.5 Hz, 3 H), 7.28−7.25 (m, 3 H), 7.21 (s, 1 H), 7.15−7.12 (m, 2 H), 6.90−6.88 (m, 2 H), 5.50 (d, *J* = 5 Hz, 1 H), 5.00 (d, *J* = 5 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.9, 165.4, 156.7, 145.8, 138.6, 134.3, 131.6, 131.5, 130.1, 129.1, 127.9, 126.5, 116.4, 116.2, 73.3, 71.9, 61.4, 21.7 ppm.

4: Isolated as a white solid (294 mg, 78% yield). M.p. 95−97 °C. IR (deposit from CH_2Cl_2 solution on NaCl plate): $\tilde{\nu}$ = 1715 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.46 Hz, 2 H), 7.41 (d, *J* = 8.46 Hz, 2 H), 7.21 (s, 1 H), 3.99 (s, 1 H), 2.47 (s, 3 H), 1.21 (s, 3 H), 0.89 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.5, 153.5, 146.1, 133.2, 130.4, 127.6, 70.4, 61.7, 30.7, 27.8, 23.2, 21.7 ppm.

5: Isolated as a white solid (292 mg, 70% yield). M.p. 138−140 °C. IR (deposit from CH_2Cl_2 solution on NaCl plate): $\tilde{\nu}$ = 1685 (C=O) cm^{-1}, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78−7.74 (m, 2 H), 7.38−7.34 (m, 2 H), 7.21 (s, 1 H), 6.13 (s, 1 H), 4.10 (s, 1 H), 2.45 (s, 3 H), 2.09 (d, *J* = 1 Hz, 3 H), 1.88 (d, *J* = 1 Hz, 3 H), 1.20 (s, 3 H), 1.01 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.1, 160.6, 153.4, 145.6, 133.9, 130.1, 127.8, 120.1, 76.7, 70.5, 62.0, 30.7, 28.2, 23.4, 21.7, 21.2 ppm.

6: Isolated as a colorless oil (237 mg, 74% yield). HRMS: MH+: 374.1419, calculated: 374.1424. IR (deposit from CH_2Cl_2 solution on NaCl plate): $\tilde{\nu}$ = 1716 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69−7.66 (m, 2 H), 7.54−7.50 (m, 1 H), 7.44−7.41 (m, 4 H), 7.27−7.28 (m, 2 H), 4.22 (s, 1 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.22 (s, 3 H), 0.91 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.3, 156.0, 145.1, 134.0, 131.1, 129.8, 129.6, 127.8, 127.8, 76.6, 69.9, 31.2, 28.3, 24.3, 21.6 ppm.

7: Isolated as a colorless oil (212 mg, 63% yield). HRMS: MH+: 337.1579, calculated: 337.158. IR (deposit from CH_2Cl_2 solution on NaCl plate): $\tilde{\nu}$ = 1716 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74−7.71 (m, 2 H), 7.37 (d, *J* = 8 Hz, 2 H), 3.99 (s, 1 H), 3.33 (septet, *J* = 7 Hz, 1 H), 2.45 (s, 3 H), 2.27 (s, 3 H), 1.33 (d, *J* = 6.5 Hz, 3 H), 1.20 (d, *J* = 6.5 Hz, 3 H), 1.11 (s, 3 H), 0.88 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.5, 161.8, 145.0, 134.8, 130.1, 127.3, 76.1, 68.8, 31.5, 28.4, 28.0, 24.0, 22.2, 21.6, 19.8 ppm.

8: Isolated as a colorless oil (250 mg, 61% yield). IR (deposit from CH_2Cl_2 solution on NaCl plate): $\tilde{\nu}$ = 1685 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66−7.64 (m, 2 H), 7.51−7.48 (m, 1 H), 7.44−7.38 (m, 4 H), 7.26−7.24 (m, 2 H), 6.37 (s, 1 H), 4.31 (s, 1 H), 2.42 (s, 3 H), 2.24 (s, 3 H), 2.00 (s, 3 H), 1.21 (s, 3 H), 0.98 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.0, 159.8, 156.0, 144.8, 134.7, 130.9, 129.6, 129.5, 127.9, 127.8, 120.9, 76.5, 69.9, 31.2, 28.3, 24.4, 21.6, 21.3 ppm.

9: Isolated as a colorless oil (278 mg, 74% yield). IR (deposit from CH_2Cl_2 solution on NaCl plate): $\tilde{\nu}$ = 1683 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70−7.75 (m, 2 H), 7.36−7.34 (m, 2 H), 6.17 (s, 1 H), 4.10 (s, 1 H), 3.29 (septet, *J* = 7 Hz, 1 H), 2.44 (s, 3 H), 2.18 (d, *J* = 1 Hz, 3 H), 1.94 (d, *J* = 1 Hz, 3 H), 1.29 (d, *J* = 7 Hz, 3 H), 1.20 (d, *J* = 7 Hz, 3 H), 1.10 (s, 3 H), 0.95 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.3, 161.8, 159.1, 144.7,

135.5, 129.9, 127.4, 120.8, 76.0, 68.7, 31.5, 28.3, 28.2, 24.1, 22.1, 21.6, 21.2, 19.9 ppm.

Acknowledgments

We gratefully acknowledge financial support from the Robert A. Welch Foundation (Grant No. D-1361) and NIH (GM-60261), and Texas Excellence Fund Fellowships for D. Chen and C. Timmons.

[1] [1a] I. Ojima, in: *The Organic Chemistry of* β-*Lactams* (Ed.: G. I. Georg); VCH Publishers: New York, **1992**; pp. 197−255. [1b] I. Ojima, *Acc. Chem. Res.* **1995**, *28*, 385−389.

[2] [2a] D. Lucet, T. Le Gall, C. Mioskowski, *Angew. Chem. Int. Ed.* **1998**, *37*, 2580−2627. [2b] A. Vico, R. Fernandez de la Pradilla, *Recent Res. Devel. Org. Chem.* **2000**, *4*, 327−334, (Transworld Research Network, Trivandrum-8).

[3] [3a] E. J. Corey, D.-H. Lee, S. Sarshar, *Tetrahedron: Asymmetry* **1995**, *6*, 3−6. [3b] A. O. Chong, K. Oshima, K. B. Sharpless, *J. Am. Chem. Soc.* **1977**, *99*, 3420−3426. [3c] M. Reetz, R. Jaeger, R. Drewlies, M. M. Hubel, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 103−105. [3d] T. Hayashi, E. Kishi, V. A. Soloshonok, Y. Uozumi, *Tetrahedron Lett.* **1996**, *37*, 4969−4972. [3e] M. E. Solomon, C. L. Lynch, D. H. Rich, *Tetrahedron Lett.* **1995**, *36*, 4955−4958.

[4] [4a] S. E. Denmark, X. Su, Y. Nishigaichi, D. M. Coe, K.-T. Wong, S. B. D. Winter, J. Y. Choi, *J. Org. Chem.* **1999**, *64*, 1958−1967. [4b] H. Han, J. Yoon, K. D. Janda, *J. Org. Chem.* **1998**, *63*, 2045−2047. [4c] P. F. Richardson, L. T. J. Nelson; K. B. Sharpless, *Tetrahedron Lett.* **1995**, *36*, 9241−9244. [4d] P. O'Brien, T. D. Towers, *J. Org. Chem.* **2002**, *67*, 304−307. [4e] A. Alexakis, I. Aujard, P. Mangeney, *Synlett* **1998**, 873−874. [4f] R. D. Dghaym, R. Dhawan, B. A. Arndtsen, *Angew. Chem. Int. Ed.* **2001**, *40*, 3228−3230.

[5] [5a] W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, *J. Am. Chem. Soc.* **1990**, *112*, 2801−2802. [5b] L. Deng, E. N. Jacobsen, *J. Org. Chem.* **1992**, *57*, 4320−4523. [5c] R. Irie, K. Noda, Y. Ito, N. Matsumoto, Y. Katsuki, *Tetrahedron Lett.* **1990**, *31*, 7345−7348. [5d] R. Irie, Y. Ito, Y. Katsuki, *Synlett* **1991**, 265−266.

[6] [6a] K. Muniz, M. Nieger, *Synlett* **2003**, 211−214. [6b] E. Backvall, *Tetrahedron Lett.* **1975**, 2225−2228. [6c] O. Chang, K. Oshima, K. B. Sharpless, *J. Am. Chem. Soc.* **1977**, *99*, 3420−3421. [6d] J. Barluenga, L. Alonsocires, G. Asensio, *Synthesis* **1981**, 376−378. [6e] J. Barluenga, F. Aznar, M. C. S. de Mattos, W. B. Kover, S. Garcia-Granda, E. Perez-Carreno, *J. Org. Chem.* **1991**, *56*, 2930−2932. [6f] For a two-step synthesis of non-chlorinated imidazolines (25−36% yields) see: B. Crookes, T. P. Seden, R. W. Turner, *J. Chem. Soc., Chem. Commun.* **1968**, 342.

[7] G. Li, H.-X. Wei, S. H. Kim, M. D. Carducci, *Angew. Chem. Int. Ed.* **2001**, *40*, 4277−4280.

[8] [8a] H.-X. Wei, S. H. Kim, G. Li, *J. Org. Chem.* **2002**, *67*, 4777−4781. [8b] G. Li, H.-X. Wei, S. H. Kim, *Tetrahedron Lett.* **2000**, *41*, 8699−8701. [8c] D. Chen, C. Timmons, H.-X. Wei, G. Li, *J. Org. Chem.* **2003**, *68*, 5742−5745.

[9] H.-X. Wei, S. Siruta, G. Li, *Tetrahedron Lett.* **2002**, *43*, 3809−3812.

[10] V. Thakur, S. Talluri, A. Sudalai, *Org. Lett.* **2003**, *5*, 861−864.

[11] [11a] G. Li, H.-X. Wei, S. H. Kim, M. Neighbors, *Org. Lett.* **1999**, *1*, 395−397. [11b] G. Li, H.-X. Wei, S. H. Kim, *Org. Lett.* **2000**, *2*, 2249−2252.

[12] [12a] G. Li, H.-X. Wei, S. H. Kim, *Tetrahedron* **2001**, *57*, 8407−8411. [12b] H.-X. Wei, S. H. Kim, G. Li, *Tetrahedron* **2001**, *57*, 3869−3973.

Received May 28, 2003

