DOI: 10.1002/ejoc.200600020

Regio- and Stereoselective Synthesis of *anti*-1,3-Diaryl-3-chloro-2-(*o*-nitrophenylsulfonylamino)-3-propan-1-ones through Catalytic Aminohalogenation Reaction of α,β-Unsaturated Ketones

Junying Liu,[a] Yining Wang,[a] and Guigen Li*[a]

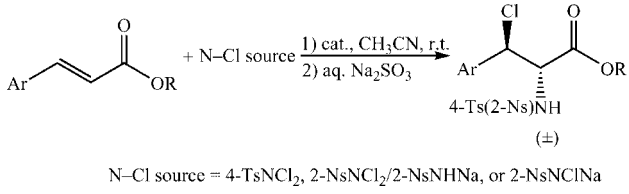
Keywords: Aminohalogenation / Haloamine / Copper(I) triflate

The synthesis of *anti*-1,3-diaryl-3-chloro-2-(2-nitrophenylsulfonylamino)-3-propan-1-ones has been achieved. The aminohalogenation of α,β-unsaturated ketones resulted in the vicinal haloamine products in high regio- and stereoselectivity and modest to good chemical yields. The reaction can be conducted under convenient conditions by using the combination of 2-$NsNCl_2$/2-NsNHNa (2-Ns = 2-nosyl = 2-nitrophenylsulfonyl) as the nitrogen/chlorine source and by using copper(I) triflate as the catalyst. An *N*-(2-nosyl)-*N*-H-aziridinium intermediate was proposed to exist in the aminohalogenation process.

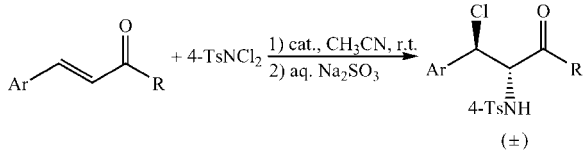
Introduction

The vicinal haloamine functionalities present a very useful structural moiety in synthetic organic chemistry.[1–6] They have potentials to be converted into dehydroamino acids, aziridines and many other important organic products through intramolecular or intermolecular nucleophilic displacements of the β-chlorine atom.[7–9] Although great progress has been made in developing efficient synthetic approaches to this functionality, it continuously provides both academic and industrial challenges.[7–9]

In the past several years, a regio- and stereoselective aminohalogenation of α,β-unsaturated esters has been developed by the use of several different nitrogen/chlorine sources such as 4-$TsNCl_2$, 2-NsNNaCl, or the combination of 2-$NsNCl_2$ and 2-NsNHNa in the presence of metal catalysts (Scheme 1).[7–9] However, the aminohalogenation of α,β-unsaturated ketones has not been developed until very recently when our group reported the aminohalogenation of α,β-unsaturated ketones by using easily available 4-$TsNCl_2$ as the nitrogen/chlorine source (Scheme 2).[7c] In the continuing study, 2-nitrophenylsulfonyl was designed as the protecting group for the resulting haloamino products in place of their 4-tolylsulfonyl-protected counterparts. The advantage of such a modification is the easier cleavage of the nitrophenylsulfonyl group by using PhSH and K_2CO_3 in DMF at room temperature.[10–13] In addition, 2-$NsNCl_2$ is much more stable than 4-$TsNCl_2$. Essentially, the former can be stored at room temperature without special gas protection for several months.



Scheme 1.



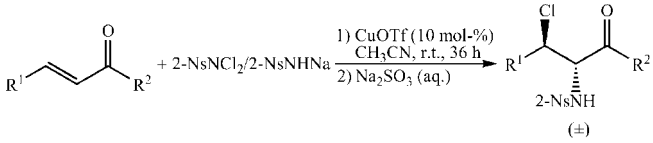
Scheme 2.

Results and Discussion

Due to the structural similarity of α,β-unsaturated ketones to their ester counterparts, as well as their similar behaviors in our previous work,[7,8] the catalytic aminochlorination was conducted by utilizing 2-NsNNaCl and the combination of 2-$NsNCl_2$ and 2-NsNHNa as the nitrogen/halogen sources. For the initial study, chalcone was chosen as the substrate. The first attempt to treat chalcone with 2-NsNNaCl as the nitrogen/chlorine source in the presence of copper(I) triflate catalysts gave poor results in terms of chemical yield and stereoselectivity. However, a good result was obtained when the combination of the nitrogen/chlorine source of 2-NsNHNa/2-$NsNCl_2$ was utilized with the same catalytic system. The reaction reached completion at room temperature in about 36 h, and the haloamine product was obtained in a chemical yield of 50% and high stereo-

[a] Department of Chemistry and Biochemistry, Texas Tech University,
Lubbock, TX 79409-1061, USA

selectivity (*anti*/*syn* = 7:1) (Scheme 3). On the basis of these encouraging results, a series of common α,β-unsaturated ketones were then systematically investigated. Under these conditions, good to excellent yields and stereoselectivities were obtained (Table 1).

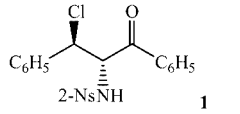
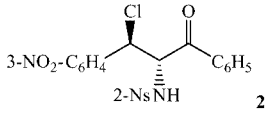
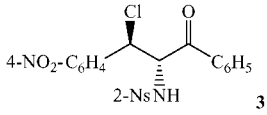
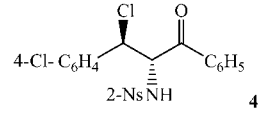
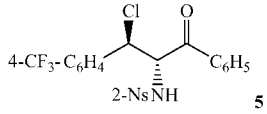
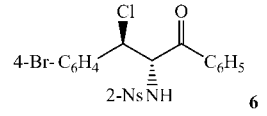
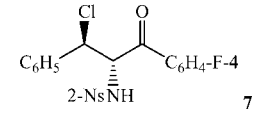
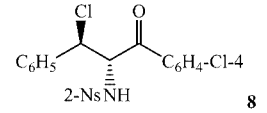
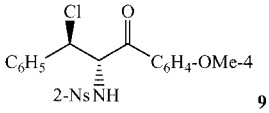


Scheme 3.

For each of these cases, there is no minor regioisomer detected; therefore, the regioselectivity can be completely controlled. Meanwhile, good to excellent stereoselectivities (7:1 to 20:1) have been achieved for all of these substrates. The chemical yields of these α,β-unsaturated ketones are lower than those of α,β-unsaturated esters as reported by our group previously.[8] For the new process both 2-NsNHNa and $Cu^{I}OTf$ are crucial to inhibit the competing diamination reaction.

This reaction is suggested to proceed through the formation of an aziridinium intermediate at its initial step, which is similar to that of the previous α,β-unsaturated ester system.[7,8,14] Besides 2-$NsNCl_2$ as the direct electrophilic

Table 1. Results of the aminohalogenation reaction of α,β-unsaturated ketones.

Entry	R^1	R^2	Product (±)	Yield[a] (%)	Stereoselectivity[b] (*anti*/*syn*)
1	C_6H_5	C_6H_5	 **1**	50	7:1
2	3-NO_2-C_6H_4	C_6H_5	 **2**	74	20:1
3	4-NO_2-C_6H_4	C_6H_5	 **3**	72	10:1
4	4-Cl-C_6H_4	C_6H_5	 **4**	52	9:1
5	4-CF_3-C_6H_4	C_6H_5	 **5**	75[c]	7:1
6[d]	4-Br-C_6H_4	C_6H_5	 **6**	51	20:1
7	C_6H_5	4-F-C_6H_4	 **7**	58	15:1
8[d]	C_6H_5	4-Cl-C_6H_4	 **8**	44	7:1
9	C_6H_5	4-MeO-C_6H_4	 **9**	41	15:1

[a] Yields after purification by flash chromatography. [b] Estimated by ^{1}H NMR determinationof the crude product. [c] Decomposed during purification, the yield was estimated by ^{1}H NMR determination of the crude product by comparison with a standard. [d] The reaction was conducted on a 0.5 mmol scale.

amination species to give an *N*-chloro-*N*-(2-nosyl)aziridinium intermediate [Figure 1 (a)], its monochloro counterpart 2-NsNHCl, which could be generated from the reaction of 2-$NsNCl_2$ with 2-NsNHNa, can also act as the electrophilic amination species to give protonated an *N*-nosyl-*N*-H-aziridinium intermediate [Figure 1 (b)]. The above two aziridinium intermediates can be opened by Cl^- in an S_N2 manner which is responsible for the excellent *anti* stereoselectivity. The regioselectivity can be explained by the fact that the β-position of the aziridinium intermediates (a) and (b) has more positive charge than the α-position because of the stabilization effect from the phenyl ring. 2-NsNHNa could be benefitial to the reaction in two manners, to control the ionic strength and to generate the Cl–N source as mentioned previously.

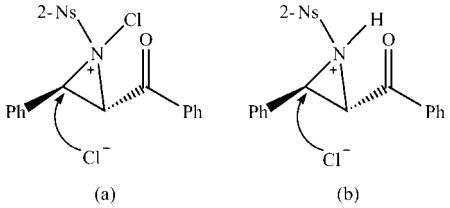


Figure 1. Two possible aziridinium intermediates.

This aziridinium-based hypothesis is strongly supported by the electrophilic diamination reaction in the absence of any catalyst where the diamines were produced predominantly.[14] Very recently, the Hammet effect of the aminohalogenation reaction has been studied by using methylenecyclopropanes as the substrate.[15] A set of parallel aminohalogenation experiments of a variety of methylenecyclopropanes bearing various substituents on their benzene rings were performed under consistent conditions. The linear free-energy relationship of the reaction was plotted, and a straight line was obtained with a ρ value of –1.35, which strongly implies the existence of a positive ion intermediate during the aminohalogenation reaction process. In addition, when the aminohalogenation was carreid out with an 2-$NsNCl_2$/NaI mixture as the nitrogen and halogen source, the vicinal aminoiodination product was exclusively produced. The above evidence cannot support the possibility of a bridged chloronium ion mechanism.

In conclusion, a highly regio- and stereoselective aminohalogenation of enones has been developed by using the combination of 2-$NsNCl_2$/2-NsNHNa as the nitrogen/chlorine source and copper(I) triflate as the catalyst. The reaction is very convenient to perform in acetonitrile at room temperature. This process provides a first synthetic approach to *N*-(2-nosyl)haloamino ketones in which the protecting group can be readily cleaved under mild conditions.

Experimental Section

General Procedure: All reactions were performed in oven-dried vials. Acetonitrile was dried and freshly distilled immediately prior to use. Flash chromatography was performed using silica gel (Merck 60, 230–400 mesh). ^1H and ^{13}C NMR spectra were obstained with Varian Inova 500 MHz and Varian Mercury Plus 300 MHz spectrometers using deuterated chloroform as solvent. Internal TMS (δ = 0.0 ppm) was used as the reference for ^1H NMR, while the deuterated chloroform solvent (δ = 77.0 ppm) was used as the reference for ^{13}C NMR. Melting points are reported uncorrected. FT-IR spectra were obtained with Nicolet IR 100 or Perkin–Elmer Series 1600 spectrometers. High-resolution mass spectrometry was performed at the Scripps Center for Mass Spectrometry.

Typical Procedure for Aminohalogenation of α,β-Unsaturated Ketones: Into a dry vial was added chalcone (208 mg, 1.0 mmol) and freshly distilled acetonitrile (3.0 mL). Under stirring, 2-$NsNCl_2$ (407 mg, 1.5 mmol), 2-NsNHNa (672 mg, 3.0 mmol), and copper(I) trifluoromethanesulfonate–benzene complex (50 mg, 0.1 mmol, 10 mol-%) were added. The resulting dark brown solution in the capped vial was stirred at room temperature for 36 h. As the reaction proceeded to completion over 36 h, the reaction was quenched by addition of saturated aqueous Na_2SO_3 solution (4 mL). The phases were separated, and the aqueous phase was extracted with ethyl acetate (three times). The combined organic layers were washed with water and brine, dried with anhydrous magnesium sulfate, and concentrated to dryness. Purification by flash chromatography (EtOAc/hexane, 3:7, v/v) provided the product.

3-Chloro-1,3-diphenyl-2-(2-nosylamino)propan-1-one (1): Isolated as yellow oil (223 mg, 50% yield). IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3312 (N–H), 1681 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.90–7.84 (m, 2 H), 7.82–7.74 (m, 2 H), 7.66–7.52 (m, 2 H), 7.50–7.39 (m, 3 H), 7.31–7.24 (m, 2 H), 7.22–7.16 (m, 3 H), 6.46–6.35 (d, *J* = 9.5 Hz, 1 H), 5.77–5.67 (dd, *J* = 7.0, 9.5 Hz, 1 H), 5.27–5.19 (d, *J* = 7.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 195.20, 147.11, 135.78, 135.22, 134.35, 134.31, 133.40, 132.80, 129.97, 129.26, 128.94, 128.81, 128.55, 127.93, 125.46, 62.20, 61.42, 31.56 ppm. HRMS: calcd. for [MH^+] 445.0619, found 445.0623.

3-Chloro-3-(3-nitrophenyl)-2-(2-nosylamino)-1-phenylpropan-1-one (2): Isolated as white solid (360 mg, 74% yield); m.p. 103–105 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3303 (N–H), 1684 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.13–8.067 (m, 2 H), 7.92–7.85 (m, 2 H), 7.84–7.76(m, 2 H), 7.75–7.70 (m, 1 H), 7.68–7.61 (m, 1 H), 7.61–7.55 (m, 1 H), 7.54–7.41(m, 4 H), 6.47–6.36 (d, *J* = 9.5 Hz, 1 H), 5.77–5.67 (dd, *J* = 7.5, 9.5 Hz, 1 H), 5.35–5.25 (d, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 194.90, 147.98, 147.14, 138.23, 134.97, 134.74, 134.31, 133.99, 133.77, 132.76, 129.91, 129.62, 129.11, 128.89, 125.58, 124.13, 123.20, 109.88, 61.71 ppm. HRMS: calcd. for [MH^+] 490.047, found 490.0490.

3-Chloro-3-(4-nitrophenyl)-2-(2-nosylamino)-1-phenylpropan-1-one (3): Isolated as white solid (351 mg, 72% yield); m.p. 180–182 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3305 (N–H), 1686 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.08–8.02 (m, 2 H), 7.94–7.89 (m, 2 H), 7.81–7.72 (m, 2 H), 7.68–7.62 (m, 1 H), 7.59–7.51 (m, 3 H), 7.51–7.45 (t, 2 H), 7.45–7.36 (m, 1 H), 6.52–6.43 (d, *J* = 10.0 Hz, 1 H), 5.76–5.66 (dd, *J* = 8.0, 9.5 Hz, 1 H), 5.34–5.26 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 194.99, 148.09, 147.07, 143.11, 134.93, 134.77, 133.94, 133.71, 132.70, 129.92, 129.27, 129.07, 128.92, 125.44, 123.64, 61.44, 59.80 ppm. HRMS: calcd. for [MH^+] 490.047, found 490.0478.

3-Chloro-3-(4-chlorophenyl)-2-(2-nosylamino)-1-phenylpropan-1-one (4): Isolated as white solid (249 mg, 52% yield); m.p. 158–160 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3316 (N–H), 1692 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.98–7.90 (m, 2 H), 7.83–7.76 (m, 1 H), 7.75–7.68 (m, 1 H), 7.68–7.57 (m, 2

H), 7.54–7.43 (m, 3 H), 7.25–7.19 (m, 2 H), 7.15–7.08 (m, 2 H), 6.36–6.26 (d, J = 10.0 Hz, 1 H), 5.72–5.64 (dd, J = 8.0, 9.5 Hz, 1 H), 5.20–5.11 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 195.31, 147.02, 135.16, 135.11, 134.66, 134.54, 134.27, 133.43, 132.90, 129.84, 129.43, 129.03, 128.94, 128.76, 125.43, 61.69, 60.42 ppm. HRMS: calcd. for [MH$^+$] 479.023, found 479.0250.

3-Chloro--2-(2-nosylamino)-1-phenyl-3-[4-(trifluoromethyl)phenyl]-propan-1-one (5): Isolated as white solid; m.p. 128–130 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3304 (N–H), 1685 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.91–7.86 (m, 2 H), 7.80–7.73 (m, 2 H), 7.66–7.60 (m, 1 H), 7.60–7.54 (m, 1 H), 7.50–7.40 (m, 7 H), 6.48–6.36 (d, J = 9.5 Hz, 1 H), 5.79–5.68 (dd, J = 8.0, 9.5 Hz, 1 H), 5.33–5.15 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 195.08, 147.09, 140.02, 135.08, 134.59, 134.10, 133.72, 132.81, 131.33, 131.07, 129.80, 129.02, 128.87, 128.56, 125.50, 125.47, 125.43, 61.62 ppm. HRMS: calcd. for [MH$^+$] 513.0493, found 513.0508.

3-(4-Bromophenyl)-3-chloro-2-(2-nosylamino)1-phenylpropan-1-one (6): Isolated as white solid (133 mg, 51% yield); m.p. 178–180 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3303 (N–H), 1682 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.99–7.91 (m, 2 H), 7.84–7.77 (m, 1 H), 7.75–7.69 (m, 1 H), 7.68–7.60 (m, 2 H), 7.54–7.44 (m, 3 H), 7.30–7.22 (m, 2 H), 7.20–7.12 (m, 2 H), 6.39–6.27 (d, J = 10.0 Hz, 1 H), 5.75–5.61 (dd, J = 8.0, 10.0 Hz, 1 H), 5.18–5.10 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 195.33, 146.99, 135.20, 135.10, 134.55, 134.24, 133.46, 132.95, 131.68, 129.82, 129.71, 129.03, 128.96, 125.44, 123.48, 61.58, 60.46 ppm. HRMS: calcd. for [MH$^+$] 522.9725, found 522.9717.

3-Chloro-1-(4-fluorophenyl)-2-(2-nosylamino)-3-phenylpropan-1-one (7): Isolated as white solid (268 mg, 58% yield); m.p. 52–54 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3315 (N–H), 1681 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.95–7.89 (m, 2 H), 7.82–7.73 (m, 2 H), 7.61–7.558 (m, 1 H), 7.49–7.43 (m, 1 H), 7.30–7.24 (m, 2 H), 7.20–7.15 (m, 3 H), 7.15–7.09 (m, 2 H), 6.42–6.33 (d, J = 9.5 Hz, 1 H), 5.72–5.63 (dd, J = 7.5, 9.5 Hz, 1 H), 5.23–5.16 (d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 193.81, 147.07, 135.83, 134.33, 133.43, 132.87, 131.70, 131.62, 129.91, 129.31, 128.56, 127.92, 125.49, 116.26, 116.09, 61.88, 61.49 ppm. HRMS: calcd. for [MH$^+$] 463.0525, found 463.0524.

3-Chloro-1-(4-chlorophenyl)-2-(2-nosylamino)-3-phenylpropan-1-one (8): Isolated as white solid (104 mg, 44% yield); m.p. 156–158 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3311 (N–H), 1685 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.87–7.78 (m, 3 H), 7.78–7.72 (m, 1 H), 7.63–7.55 (m, 1 H), 7.52–7.45 (m, 1 H), 7.45–7.39 (m, 2 H), 7.31–7.23 (m, 2 H), 7.23–7.14 (m, 3 H), 6.43–6.33 (d, J = 9.5 Hz, 1 H), 5.70–5.60 (dd, J = 7.5, 9.5 Hz, 1 H), 5.24–5.15 (d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 194.34, 147.07, 141.03, 135.78, 134.33, 133.64, 133.45, 132.89, 130.20, 129.92, 129.34, 129.27, 128.60, 127.91, 125.51, 61.95, 61.44 ppm. HRMS: calcd. for [MH$^+$] 479.023, found 479.0229.

3-Chloro-1-(4-methoxyphenyl)-2-(2-nosylamino)-3-phenylpropan-1-one (9): Isolated as white solid (196 mg, 41% yield); m.p. 100–102 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate): $\tilde{\nu}$ = 3313 (N–H), 1673 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.89–7.84 (m, 2 H), 7.81–7.73 (m, 3 H), 7.60–7.52 (m, 1 H), 7.47–7.40 (m, 1 H), 7.32–7.25 (m, 5 H), 7.25–7.15 (m, 3 H), 6.99–6.91 (m, 2 H), 6.41–6.31 (d, J = 9.5 Hz, 1 H), 5.70–5.63 (dd, J = 8.0, 9.5 Hz, 1 H), 5.24–5.16 (d, J = 7.0 Hz, 1 H), 3.90 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 193.21, 147.14, 136.00, 134.43, 133.30, 132.72, 131.34, 129.96, 129.21, 128.52, 128.09, 128.00, 127.69, 125.44, 114.20, 61.86, 61.55, 55.65 ppm. HRMS: calcd. [MH$^+$] 475.0725, found 475.0730.

Acknowledgments

We gratefully acknowledge the National Institutes of Health (CA 99995-1) and the Robert A. Welch Foundation (D-1361) for the generous support of this work. We thank Cody Timmons and Sri Kotti for their assistance.

[1] J. E.G. Kemp, in: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, vol. 3, p. 471–513.
[2] a) D. A. Griffith, S. J. Danishefsky, *J. Am. Chem. Soc.* **1991**, *113*, 5863–5870; b) D. H. R. Barton, M. R. Britten-Kelly, D. Ferreira, *J. Chem. Soc., Perkin Trans. 1* **1978**, 1090–1100; c) H. Driguez, J.-P. Vermes, J. Lessard, *Can. J. Chem.* **1978**, *56*, 119–130; d) J. Lessard, H. Driguez, J.-P. Vermes, *Tetrahedron Lett.* **1970**, *11*, 4887–4891.
[3] F. A. Daniher, P. E. Butler, *J. Org. Chem.* **1968**, *33*, 2637–2642.
[4] A. Klepacz, A. Zwierzak, *Tetrahedron Lett.* **2001**, *42*, 4539–4540.
[5] a) F. A. Daniher, P. E. Bulter, *J. Org. Chem.* **1968**, *33*, 4336–4343; b) F. A. Daniher, M. T. Melchior, P. W. Butler, *Chem. Commun. (London)* **1968**, 931–932.
[6] T. P. Seden, R. W. Turner, *J. Chem. Soc. C* **1968**, 876–878.
[7] a) X. Xin, S. R. S. S. Kotti, J.-Y. Liu, J. F. Cannon, A. D. Headley, G. Li, *Org. Lett.* **2004**, *6*, 4881–4884; b) S. R. S. S. Kotti, X. Xu, Y. N. Wang, A. D. Headley, G. Li, *Tetrahedron Lett.* **2004**, *45*, 7209–7212; c) D. Chen, C. Timmons, S. Chao, G. Li, *Eur. J. Org. Chem.* **2004**, 3097–3101.
[8] a) H.-X. Wei, S. H. Kim, G. Li, *Tetrahedron* **2001**, *57*, 3869–3873; b) G. Li, H.-X. Wei, S. H. Kim, *Org. Lett.* **2000**, *2*, 2249–2252; c) G. Li, H.-X. Wei, S. H. Kim, M. Neighbors, *Org. Lett.* **1999**, *1*, 395–397.
[9] a) X. Qi, S. H. Lee, J. Y. Kwon, Y. Kim, S. J. Kim, Y. S. Lee, J. Yoon, *J. Org. Chem.* **2003**, *68*, 9140–9143; b) V. V. Thakur, S. K. Talluri, A. Sudalai, *Org. Lett.* **2003**, *5*, 861–864; c) A. Volonterio, P. Bravo, W. Panzeri, C. Pesenti, M. Zanda, *Eur. J. Org. Chem.* **2002**, 3336–3340; d) S. Raghavan, S. R. Reddy, K. A. Tony, C. N. Kumar, S. Nanda, *Synlett* **2001**, *6*, 851–853; e) M. R. Manzoni, T. P. Zabawa, D. Kasi, S. R. Chemler, *Organometallics* **2004**, *23*, 5618–5621.
[10] T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett.* **1995**, *36*, 6373–6374.
[11] S. G. Nelson, K. L. Spencer, *Angew. Chem. Int. Ed.* **2000**, *39*, 1323–1325.
[12] P. Wipf, T. C. Henninger, *J. Org. Chem.* **1997**, *62*, 1586–1587.
[13] S. C. Miller, T. S. Scanlan, *J. Am. Chem. Soc.* **1997**, *119*, 2301–2302.
[14] For recent diaminations, see: a) G. Li, H.-X. Wei, S. H. Kim, M. D. Carducci, *Angew. Chem. Int. Ed.* **2001**, *40*, 4277–4280; b) H.-X. Wei, S. H. Kim, G. Li, *J. Org. Chem.* **2002**, *67*, 4777–4781; c) K. I. Booker-Milburn, D. J. Guly, B. Cox, P. A. Procopiou, *Org. Lett.* **2003**, *5*, 3313–3315; d) K. Muniz, M. Nieger, *Synlett* **2003**, 211–214; e) D. Chen, C. Timmons, H.-X. Wei, G. Li, *J. Org. Chem.* **2003**, *68*, 5742–5745; f) C. Timmons, D. Chen, X. Xu, G. Li, *Eur. J. Org. Chem.* **2003**, 3850–3854; g) W. Pei, H.-X. Wie, A. D. Headley, G. Li, *J. Org. Chem.* **2003**, *68*, 8404–8408.
[15] Q. Li, M. Shi, C. Timmons, G. Li, *Org. Lett.* **2006**, *8*, 625–628.

Received: January 11, 2006
Published Online: May 17, 2006

