The First Synthesis of Enantiopure α-Amino Ketimines and Amino Aziridines

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Chiral 1-aminoalkyl chloromethyl ketimines **2** are synthesized in enantiomerically pure form starting from 1-aminoalkyl chloromethyl ketones **1** and different amines. Reduction of amino ketimines **2** and subsequent spontaneus cyclization affords aminoalkyl aziridines **3** with high diastereoisomeric excess and without detectable racemization.

Introduction

While optically active α-amino aldimines have been widely used as chiral building blocks in organic synthesis,[1] the synthesis of the corresponding α-amino ketimines remains unreported.[2] Another attractive starting material for further chemical transformations, yielding products of predetermined stereo- and regiochemistry,[3] is the chiral aziridine ring, which has been used to obtain a variety of biologically important molecules such as amino acids, *β*-lactams, and alkaloids.[4] The synthesis of the chiral aziridine ring[5] is generally achieved starting from enantiomerically pure natural compounds (amino acids, carbohydrates, hydroxy acids)[4d,e] or by direct aziridination of C=C[6] or C=N[7] bonds. However, preparation from available enantiopure natural products typically requires a multistep transformation;[8] aziridination of alkenes is limited by its moderate enantiomeric excess and poor generality,[9] while aziridination of C=N suffers from difficulty in varying the N-substituent, from the fact that only aldimines can be used as starting materials, and because moderate enantioselectivity is obtained.[7] These drawbacks have seriously restricted the use of the chiral aziridine ring in organic synthesis.

In addition, although functionalized aziridines (for example, hydroxyaziridines and aziridine-2-carboxylates) have been reported, enantiopure amino aziridines remain unreported[10] even though their synthesis possibly could furnish a new access to chiral 1,2-diamines.[11] Thus, the development of a simple and effective general method for preparation of enantiopure amino aziridines would be desirable.

Previously, we have described the synthesis of chiral α′-amino α-chloro ketones **1**[12] by direct reaction of easily available α-amino esters with in situ generated chloromethyllithium. We have also described some synthetic applications of these α-amino chloromethyl ketones: their

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(1) For a review of the synthesis and use of α-amino aldimines, see: (a) Reetz, M. T. *Chem. Rev.* **1999**, *99*, 1121. (b) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1531.

(2) Extensive search of the chemical literature leads us to the conclusion that no enantiopure α-amino ketimines have been described.

(3) (a) For a general review of aziridine chemistry, see: Pearson, W. H.; Lian, B. W.; Bergmeier, S. C. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: New York, 1996; Vol 1a. (b) Dauben, P.; Dubois, L.; Dau, M. E. T. H.; Dodd, R. H. *J. Org. Chem.* **1995**, *60*, 2035. (c) da Zhang, Z.; Scheffold, R. *Helv. Chim. Acta* **1993**, *76*, 2602. (d) Bodenan, J.; Chanet-Ray, J.; Vessiere, R. *Synthesis* **1992**, 288. (e) Sato, K.; Kozikowski, A. P. *Tetrahedron Lett.* **1989**, *30*, 4073.

(4) (a) Muller, P. In *Advances in Catalytic Process*: *Vol. 2 Asymmetric Catalysis*; Doyle, M. P., Ed.; JAI Press: Greenwich, CT, 1997. (b) Kump, J. E. G. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 469. (d) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599. (e) Tanner, D. *Pure Appl. Chem.* **1993**, *65*, 1319. (f) Hudlicky, T.; Seoane, G.; Price, J. D.; Gadamasetti, K. G. *Synlett* **1990**, 433.

(5) For recent review in the asymmetric synthesis of aziridines, see: Osborn, H. M. I.; Sweeney, J. *Tetrahedron*: *Asymmetry* **1997**, *8*, 1693.

(6) (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 5328. (b) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326. (c) Aires-de-Sousa, J.; Lobo, A. M.; Prabhakar, S. *Tetrahedron Lett.* **1996**, *37*, 3183. (d) Atkinson, R. S. *Tetrahedron* **1999**, *55*, 1519.

(7) (a) Aggarwal, V. K.; Thompson, A.; Jones, R. V. H.; Standen, M. C. H. *J. Org. Chem.* **1996**, *61*, 8368. (b) Li, A.; Zhou, Y.; Dai, L.; Hou, X.; Xia, L.; Lin, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1317. (c) Zhou, Y.; Li, A.; Dai, L. *Tetrahedron Lett.* **1997**, *38*, 7225. (d) Cantrill, A. A.; Hall, L. D.; Jarvis, A. N.; Osborn, H. M. I.; Raphy, J.; Swenney, J. B. *Chem. Commun.* **1996**, 2631. (e) Davis, F. A.; Liu, H.; Zhou, P.; Fang, T.; Reddy, V.; Zhang, Y. *J. Org. Chem.* **1999**, *64*, 7559.

(8) Hansen, K. B.; Finney, N. S.; Jacobsen, E. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 676.

(9) Aryl-substituted olefins (ref 7a,b) or electron-deficient alkenes (ref 7c,d) are required as starting materials.

(10) Extensive search of the chemical literature leads us to the conclusion that general methods for the synthesis of enantiopure amino aziridines and their use are not known, although they are known to a limited extent: (a) Meyer zu Reckendorf, W.; Wassiliadou-Micheli, N. *Chem. Ber.* **1970**, *103*, 37. (b) Yoshimura, J.; Iwakawa, M.; Ogura, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2506 (c) Andres, C. J.; Meyers, A. I. *Tetrahedon Lett.* **1995**, *36*, 3491. (d) Herdeis, C.; Aschenbrenner, A.; Kirfel, A.; Schwabenländer, F. *Tetrahedron*: *Asymmetry* **1997**, *8*, 2421. (e) Dollt, H.; Zabel, V. *Aust. J. Chem.* **1999**, *52*, 259.

(11) Vicinal diamines are encountered as ligands in metal-induced stereoselective reactions, in various chemotherapeutic contexts (cisplatin analogues and technetium-99 contrasting agents), as well in a wide variety of natural products: Reetz, M. T.; Jaeger, R.; Drewlies, R.; Hübel, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 103.

(12) (a) Barluenga, J.; Baragaña, B.; Alonso, A.; Concellón, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 969. (b) Barluenga, J.; Baragaña, B.; Concellón, J. M. *J. Org. Chem.* **1995**, *60*, 6696.

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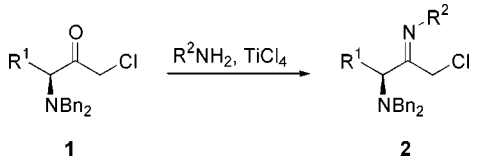
Scheme 1. Synthesis of α-Amino Ketimines



1 2

Table 1. Synthesis of α-Amino Ketimines 2

entry	product	R^1	R^2	yield[a] (%)
1	**2a**	Me	allyl	94
2	**2b**	Me	Pr	90
3	**2c**	Me	C_6H_{11}	80
4	**2d**	Me	Bn	73[b]
5	**2e**	Me	$CHPh_2$	88
6	**2f**	*i*-Bu	allyl	89
7	**2g**	*i*-Bu	Bn	86
8	**2h**	Bn	C_6H_{11}	92
9	**2i**	Bn	*p*-$MeOC_6H_4$	78
10	**2j**	Bn	Bn	74

[a] Isolated yield based on the starting ketone **1**. [b] ee >99% (see text); HPLC (Chiralcel OD-H; UV detector; 0.8 mL/min; 215 nm; 97:3 hexane/etanol; t_R = 14.3 min).

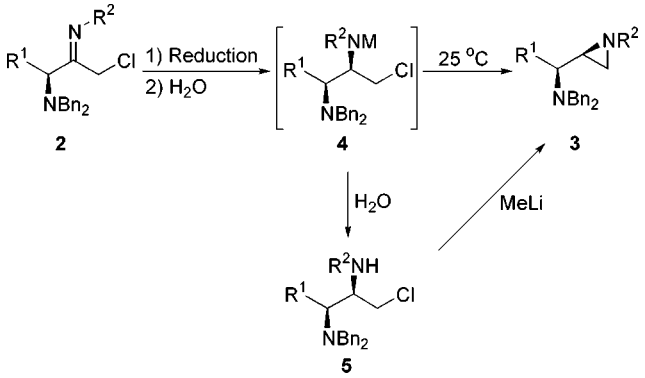
reduction gives *threo*-aminoalkyl epoxides;[12b] treatment with organometallic compounds affords 3-azetidinols;[13] their reaction with halomethyllithium leads to 2-(1-aminoalkyl) epihalohydrines.[14] We have also reported the addition of the enolates obtained from these ketones to aldehydes or ketones.[15] The high diastereoselectivity of these reactions and the enantiopurity of the compounds obtained prompted us to study new synthetic applications of chiral 1-aminoalkyl chloromethyl ketones **1** in the synthesis of enantiomerically pure building blocks. In this paper, we report the first preparation of enantiopure α-amino ketimines[16] **2** from the corresponding 1-aminoalkyl chloromethyl ketones **1** and their reduction to obtain the corresponding enantiopure amino aziridines **3**.

Results and Discussion

Synthesis of Enantiopure Ketimines 2. Reaction of 1-aminoalkyl chloromethyl ketones[12] **1** with different amines in the presence of $TiCl_4$ at room temperature gave the corresponding 1-aminoalkyl chloromethyl ketimines **2** in high yield (Scheme 1 and Table 1). Isolation of pure ketimines **2** only required removal of solvents (purity >95%, 300 MHz ^{1}H NMR spectroscopy). When amines of high boiling point were used (benzylamine, *p*-methoxyanisidine, or diphenylmethanamine), a mixture of ketimine and amine was isolated, which could be used, without further purification, to obtain the corresponding amino aziridines (see below).

Dibenzylated ketones **1** were used as starting compounds instead of other N-protected ketones due to their stability and the high diastereoselectivity they show in their reduction and reaction with organometallic compounds.[12b,13,14]

Scheme 2. Synthesis of Amino Aziridines



2 4 3 5

The obtained ketimines **2** are thermally unstable, easily hydrolyzed by acids, and only can be stored for a limited time (without solvents, 24 h at −10 °C). Despite this relative instability, compounds **2** (crude products) were characterized by NMR spectroscopy and mass spectrometry.

NMR analysis (300 MHz) of the crude reactions of α-chloroketimines **2** showed the presence of only one diastereoisomer. The *Z* stereochemistry of the imino function was determined by NOE experiments with compound **2e**. Irradiation of the hydrogen C*H*Ph_2 produced positive NOE in CH_2Cl signals, while no positive NOE was observed in the C*H*NBn_2, indicating a trans relative configuration between 1-aminoalkyl and R^2 groups, in agreement with the previously reported stereochemistry of α-amino aldimines.[1]

Synthesis of **2** proceeded with no detectable racemization. Due to the decomposition of ketimines **2** under HPLC analysis conditions, the enantiomeric purity of α-chloroketimines **2** was determined indirectly. The enantiomeric excess (ee) of chloromethyl ketone **1** (R^1 = Me), obtained after acid hydrolysis of the α-amino ketimine **2d**,[17] was >99%, showing that no racemization occurred in the synthesis and in the acid hydrolysis of ketimine **2d** and, by analogy, in all the prepared ketimines. To exclude the possibility of coelution of both enantiomers, a racemic mixture of **1** (R^1= Me) was prepared and analyzed by HPLC.

Preparation of Enantiopure Amino Aziridines 3. To prove the usefulness of enantiopure ketimines **2** in organic synthesis, these compounds were transformed into the corresponding amino aziridines by reduction. Therefore, reduction of **2** gave the amide **4**, which, after spontaneous cyclization yielded aziridines **3** (Scheme 2). Reduction of **2** was carried out using $LiAlH_4$, $NaBH_4$, or $NaBH_3CN$. Our first trials sought to determine the most suitable reducing agent. $LiAlH_4$ at −15 °C (Table 2) afforded the aziridines **3** with lower yields and diastereoisomeric excesses (de) than $NaBH_3CN$ (see below) and contaminated by other products.[18] Reduction of **2** with $NaBH_4$ at −30 °C[19] (Table 2) gave a mixture of the corresponding chloro diamines **5** (obtained by hydrolysis of **4**) and amino aziridines **3**.[20] Treatment of this mixture

(13) Barluenga, J.; Baragaña, B.; Concellón, J. M. *J. Org. Chem.* **1997**, *62*, 5974.
(14) Barluenga, J.; Baragaña, B.; Concellón, J. M. *J. Org. Chem.* **1999**, *64*, 2843.
(15) Barluenga, J.; Baragaña, B.; Concellón, J. M. *J. Org. Chem.* **1999**, *64*, 5048.
(16) No synthesis of α-amino ketimines has been reported; however, these compounds have been postulated in the reductive amination of α-amino ketones: Reetz, M. T.; Schmitz, A. *Tetrahedron Lett.* **1999**, *40*, 2741−2742.
(17) The hydrolysis of amino ketimine **2d** was carried out using an aqueous solution of acetic acid at room temperature for 5 min.
(18) When reaction was performed at lower temperature, no reduction of **2** was observed.
(19) These reaction conditions were chosen taking into account the reduction conditions of 1-aminoalkyl chloromethyl ketones using $NaBH_4$; see ref 12b.
(20) The ratios of compounds **3** and **5** were obtained from the crude reaction mixtures using ^{1}H NMR.

Table 2. Synthesis of Amino Aziridines 3 Using $NaBH_4$ or $LiAlH_4$

R^1	R^2	reaction conditions	yield[a] (%) **3**/**5**	de[b]
Me	allyl	$LiAlH_4$, −15 °C	36/−	63
Me	Pr	$NaBH_4$, −30 °C	43/11	92
Me	Pr	$NaBH_4$, 25 °C	95/−	91
Me	Pr	$LiAlH_4$, −15 °C	62/−	68
Me	Bn	$NaBH_4$, −30 °C	15/57	94
Me	$CHPh_2$	$NaBH_4$, 25 °C	47/34	92
Me	C_6H_{11}	$NaBH_4$, 25 °C	80/−	92
i-Bu	Bn	$NaBH_4$, −30 °C	35/54	>95
i-Bu	Bn	$NaBH_4$, 25 °C	87/5	>95
Bn	C_6H_{11}	$NaBH_4$, 25 °C	66/6	>95
Bn	*p*-$MeOC_6H_4$	$NaBH_4$, 25 °C	17/23[c]	>95
Bn	Bn	$NaBH_4$, −30 °C	18/65	>95
Bn	Bn	$NaBH_4$, 25 °C	92/−	>95

[a] Isolated yield based on the starting ketone **1**. [b] Diastereoisomeric excess determined by 300 MHz ^1H and ^{13}C NMR analysis of the crude products **3** and **5**. [c] Starting ketimine **2** was recovered.

Table 3. Synthesis of Enantiopure Amino Aziridines 3 Using $NaBH_3CN$

entry	**3**	R^1	R^2	yield[a] (%)	de[b]
1	**3a**	Me	allyl	60 (55)[d]	90
2	**3b**	Me	Pr	72 (60)	93
3	**3c**	Me	C_6H_{11}	85 (73)	93
4	**3d**	Me	Bn	66 (59)	95
5	**3e**	Me	$CHPh_2$	63 (58)	96
6	**3f**	*i*-Bu	allyl	74 (65)	>98
7	**3g**	*i*-Bu	Bn	90 (72)	>98
8	**3h**	Bn	C_6H_{11}	91 (73)	>95[c]
9	**3i**	Bn	*p*-$MeOC_6H_4$	74 (56)	>95[c]
10	**3j**	Bn	Bn	78 (65)	>95[c]

[a] Isolated yield based on the starting ketone **1**; yields after column chromatography are shown in parentheses. [b] Diastereoisomeric excess determined by GC/MS and 300 MHz ^1H and ^{13}C NMR analysis of the crude products **3**. [c] Diastereoisomeric excess determined by 300 MHz ^1H and ^{13}C NMR analysis of the crude products **3**. [d] ee >99%; HPLC (Chiralcel OD-H; UV detector; 0.4 mL/min; 215 nm; 199:1 hexane/ethanol; t_r = 10.6 min).

with methyllithium afforded the corresponding amino aziridines **3** as the only reaction product, the de of the reduction reaction being similar to that obtained with $NaBH_3CN$ (see below). To obtain compounds **3** directly, the reduction was carried out with $NaBH_4$ at room temperature, but, in general, compounds **3**, together with a small amount of chloro diamine **5**, were isolated (Table 2).

When $NaBH_3CN$ was used at room temperature, the corresponding amino aziridines were exclusively obtained in high yield and with high diastereoselectivity. Consequently, synthesis of amino aziridines was performed by using $NaBH_3CN$. The reaction is general, and the degree of diastereoselectivity was only moderately affected by the size of R^1 and R^2 (Table 3). The diastereoisomeric excess of amino aziridines **3** (>95%) was determined using either 300 MHz ^1H NMR or/and GC/MS analysis of crude products. Yields and diastereoisomeric excesses are summarized in Table 3.

Reduction of **2** using $NaBH_3CN$ proceeded with no detectable racemization. The enantiomeric purity of compound **3a** was determined by chiral HPLC analysis (Chiralcel OD-H) showing an ee >99%. To exclude the possibility of coelution of both enantiomers, a racemic mixture of **3a** was prepared and analyzed by HPLC.

The absolute configuration of **3e** and **3f**, as depicted in Scheme 2, was established by single-crystal X-ray analysis. The configuration of the other amino aziridines **3** was assigned by analogy. Therefore, reduction of **2** took place under nonchelation control, based on steric constraints imparted by the bulky *N*,*N*-dibenzyl protecting group. This diasterofacial preference is in agreement with that reported previously for the reduction of 1-aminoalkyl chloromethyl ketones[12b] and for the reductive amination of α-amino ketones[16] and in disagreement with the addition of organometallic compounds to aldimines.[1]

In conclusion, the reported results represent the first synthesis of enantiopure α-amino ketimines **2** with high yield from easily available materials. Reduction of these ketimines afforded directly the unreported chiral amino aziridines **3** in high yield and with high diastereoisomeric excess.

Experimental Section

General Methods. Analytical TLC was conducted in precoated silica gel 60 F-254 on aluminum sheets; compounds were visualized with UV light or iodine. ^1H NMR spectra were recorded at 300 or 200 MHz. ^{13}C NMR spectra were recorded at 75 or 50 MHz. Chemical shifts are reported in ppm relative to TMS in $CDCl_3$; coupling constants are reported in Hz. Only the molecular ions and/or base peaks in MS are given. Optical rotations were measured in $CHCl_3$. The enantiomeric purity was determined by chiral HPLC analysis using a Chiralcel OD-H (0.46 × 25 cm, Diacel) column. Flash chromatography was carried out on Merck Kiesegel 60 (230−400 mesh) using mixtures of hexane and ethyl acetate as eluents.

All reagents were purchased from Aldrich, and the amines and $TiCl_4$ were distilled before using. Chlorinated ketones **1** were prepared according to literature procedures.[12] All reactions were conducted in oven-dried glassware under dry nitrogen. All solvents were purified before using. THF and diethyl ether were distilled from sodium in a recycling still using benzophenone ketyl as indicator; methanol was distilled from magnesium turnings.

General Procedure for the Synthesis of 1-Aminoalkyl Chloromethyl Ketimines 2. A solution of $TiCl_4$ (0.06 mL, 0.55 mmol) in dry hexane (0.4 mL) was added dropwise to a stirred solution of **1** (1 mmol) in dry diethyl ether (10 mL) at −0 °C. The corresponding amine (4 mmol) was added to the resulting solution with stirring. After being stirred at room temperature for 2 h, the mixture was filtered through a pad of Celite and the solvents were removed in vacuo, yielding the corresponding crude ketimine **2**, which was used without purification.

(−)-(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-3-(allylimino)-4-chlorobutan-2-amine (2a): R_f = 0.32 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −56.4 (*c* 0.48, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41−7.34 (10 H, m), 6.03 (1 H, ddt, J = 17.2, 10.3, 5.4), 5.22 (1 H, dq, J = 17.2, 1.8), 5.13 (1 H, dq, J = 10.3, 1.8), 4.19−4.14 (3 H, m), 3.96 (1 H, d, J = 11.0), 3.67 (1 H, q, J = 6.4), 3.66 (2 × 2 H, AB syst, J = 13.5), 1.32 (3 H, d, J = 6.4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.5, 139.4, 135.4, 128.7, 128.1, 126.8, 115.1, 58.3, 54.0, 53.6, 33.6, 7.6; IR (neat) 1660, 1651; MS *m*/*z* 304 (M^+ − HCl, <1), 224 (12), 91(100); HRMS calcd for $C_{21}H_{24}N_2$ (M − HCl)$^+$ 304.1939, found 304.1944. Anal. Calcd for $C_{21}H_{25}ClN_2$: C, 73.99; H, 7.39; N, 8.22. Found: C, 73.76; H, 7.25; N, 8.20.

(−)-(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-4-chloro-3-(propylimino)butan-2-amine (2b): R_f = 0.39 (hexane/ethyl acetate 3/1); $[\alpha]^{22}_D$ = −118.1 (*c* 0.74, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz) δ 7.45−7.30 (10 H, m), 4.13 (2 H, AB syst, J = 10.8), 3.71 (1H, q, J = 6.5), 3.70 (2 × 2 H, AB syst, J = 13.5), 3.62−3.47 (2 H, m), 1.82−1.70 (2 H, m), 1.35 (3 H, d, J = 6.5), 1.03 (3 H, t, J = 7.5); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.8, 139.3, 128.6, 127.9, 126.7, 57.9, 53.8, 52.8, 33.1, 23.7, 11.7, 7.5; IR (neat) 1661; MS, *m*/*z* 306 (M^+ − HCl, <1), 224 (21), 91 (100); HRMS calcd for $C_{21}H_{26}N_2$ (M − HCl)$^+$ 306.2096, found 306.2081. Anal. Calcd for $C_{21}H_{27}ClN_2$: C, 73.56; H, 7.94; N, 8.17. Found: C, 73.68; H, 7.82; N, 8.07.

(−)-(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-4-chloro-3-(cyclohexylimino)butan-2-amine (2c): R_f = 0.52 (hexane/ethyl acetate 5/1);

$[\alpha]^{22}_D = -104.8$ (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.24 (10 H, m), 4.10 (2 H, AB syst, *J* = 10.9), 3.67−3.46 (2 H, m), 3.62 (2 × 2 H, AB syst, *J* = 13.5), 1.85−0.93 (10 H, m), 1.26 (3 H, d, *J* = 6.5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.8, 139.2, 128.4, 127.8, 126.5, 59.1, 57.1, 53.4, 33.5, 33.1, 32.9, 25.2, 24.6, 23.8, 7.4; IR (neat) 1660; MS, *m*/*z* 346 (M^+ − HCl, <1), 224 (34), 91 (100); HRMS calcd for $C_{24}H_{31}N_2$ (M − HCl)$^+$ 346.2409, found 346.2413. Anal. Calcd for $C_{24}H_{31}ClN_2$: C, 75.27; H, 8.16; N, 7.31. Found: C, 75.20; H, 8.28; N, 7.39.

(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-3-(benzylimino)-4-chlorobutan-2-amine (2d): R_f = 0.31 (hexane/ethyl acetate 10/1); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.61−7.47 (15 H, m), 4.88 (2 H, AB syst, *J* = 17.3), 4.30 (2 H, AB syst, *J* = 10.9), 3.89 (1H, q, *J* = 6.5), 3.85 (2 × 2 H, AB syst, *J* = 13.5), 1.54 (3 H, d, *J* = 6.5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.1, 139.5, 139.3, 128.6, 128.0, 127.1, 126.8, 126.3, 58.4, 54.4, 54.0, 33.8, 7.6; IR (neat) 1661; MS *m*/*z* 354 (M^+ − HCl, 2), 263 (24), 91 (100); HRMS calcd for $C_{25}H_{26}N_2$ (M − HCl)$^+$ 354.2096, found 354.2076.

(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-4-chloro-3-(diphenylmethylimino)butan-2-amine (2e): R_f = 0.44 (hexane/ethyl acetate 5/1); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.46−7.21 (20 H, m), 5.96 (1 H, s), 4.13 (2 H, AB syst, *J* = 10.9), 3.69 (1 H, q, *J* = 6.7), 3.64 (2 × 2 H, AB syst, *J* = 13.5), 1.41 (3 H, d, *J* = 6.7); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.9, 139.5, 139.3, 128.6, 128.0, 127.1, 126.8, 126.3, 67.4, 58.0, 53.9, 34.1, 7.7; IR (neat) 1660; MS, *m*/*z* 430 (M^+ − HCl, <1), 174 (57), 167 (90), 106 (91), 91 (100); HRMS calcd for $C_{31}H_{30}N_2$ (M − HCl)$^+$ 430.2409, found 430.2403.

(−)-(3*S*)-(*Z*)-*N*,*N*-Dibenzyl-2-(allylimino)-1-chloro-5-methylhexan-3-amine (2f): R_f = 0.41 (hexane/ethyl acetate 10/1); $[\alpha]^{22}_D = -105.9$ (*c* 1.07, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.27 (10 H, m), 6.00 (1 H, ddt, *J* = 17.0, 10.5, 5.2), 5.22 (1 H, dq, *J* = 17.0, 1.7), 5.10 (1 H, dq, *J* = 10.5, 1.7), 4.23−4.05 (2 H, m), 3.95 (2 H, AB syst, *J* = 10.9), 3.64 (2 × 2 H, AB syst, *J* = 13.5), 3.50−3.40 (1 H, m), 2.18−2.09 (1 H, m), 1.59−1.46 (2 H, m), 1.02 (3 H, d, *J* = 6.5), 0.90 (3 H, d, *J* = 6.5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.8, 139.7, 135.6, 128.8, 128.0, 126.8, 114.9, 60.3, 53.8, 53.2, 34.6, 30.2, 25.1, 23.8, 21.7; IR (neat) 1662, 1650; MS *m*/*z* 346 (M^+ − HCl, 1), 266 (47), 91 (100); HRMS calcd for $C_{24}H_{30}N_2$ (M − HCl)$^+$ 346.2409, found 346.2399. Anal. Calcd for $C_{24}H_{31}ClN_2$: C, 75.27; H, 8.16; N, 7.31. Found: C, 75.09; H, 8.10; N, 7.28.

(3*S*)-(*Z*)-*N*,*N*-Dibenzyl-2-(benzylimino)-1-chloro-5-methylhexan-3-amine (2g): R_f = 0.42 (hexane/ethyl acetate 10/1); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.30 (15 H, m), 4.71 (2 H, AB syst, *J* = 16.2), 4.06 (2 H, AB syst, *J* = 10.8), 3.69−3.44 (1 H, m), 3.68 (2 × 2 H, AB syst, *J* = 13.7), 2.28−2.19 (1 H, m), 1.62−1.37 (2 H, m), 1.21 (3 H, d, *J* = 6.4), 1.09 (3 H, d, *J* = 6.4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.5, 139.4, 128.5, 128.0, 127.8, 126.9, 126.2, 126.1, 60.3, 54.0, 53.6, 34.6, 30.1, 25.0, 23.6, 21.6; IR (neat) 1660; MS, *m*/*z* 396 (M^+ − HCl, <1), 266 (68), 91 (100); HRMS calcd for $C_{28}H_{32}N_2$ (M − HCl)$^+$ 396.2565, found 396.2566.

(−)-(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-4-chloro-3-(cyclohexylimino)-1-phenylbutan-2-amine (2h): R_f = 0.53 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D = -67.3$ (*c* 1.09, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42−7.23 (15 H, m), 3.84 (2 H, AB syst, *J* = 10.7), 3.72 (2 × 2 H, AB syst, *J* = 13.4), 3.60 (1 H, dd, *J* = 10.0, 2.8), 3.53−3.43 (1 H, m), 3.39 (1 H, dd, *J* = 12.8, 10.0), 2.94 (1 H, dd, *J* = 12.8, 2.8) 1.76−1.29 (10 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 140.3, 139.6, 129.6, 128.7, 128.1, 127.6, 126.8, 125.2, 63.9, 59.5, 53.6, 34.5, 33.8, 33.2, 28.0, 25.4, 24.2, 24.1; IR (neat) 1663; MS *m*/*z* 422 (M^+ − HCl, 7), 331 (26), 249 (12), 91 (100); HRMS calcd for $C_{30}H_{34}N_2$ (M − HCl)$^+$ 422.2722, found 422.2708. Anal. Calcd for $C_{30}H_{35}ClN_2$: C, 78.49; H, 7.68; N, 6.10. Found: C, 78.17; H, 7.70; N, 6.15.

(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-4-chloro-3-[(*p*-methoxyphenyl)-imino]-1-phenylbutan-2-amine (2i): R_f = 0.51 (hexane/ethyl acetate 5/1); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.43−7.21 (15 H, m), 6.88−6.58 (4 H, m), 4.03 (1 H, dd, *J* = 10.5, 3.5), 3.89 (2 × 2H, AB syst, *J* = 13.5), 3.88 (2 H, AB syst, *J* = 10.5), 3.80 (3 H, s), 3.48 (1 H, dd, *J* = 12.9, 10.5), 3.14 (1 H, dd, *J* = 12.9, 3.5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.6, 156.0, 142.3, 139.6, 139.3, 129.4, 128.6, 128.2, 127.8, 126.9, 125.4, 120.0, 114.0, 61.4, 55.1, 53.9, 35.9, 28.5; IR (neat) 1657.

(2*S*)-(*Z*)-*N*,*N*-Dibenzyl-3-(benzylimino)-4-chloro-1-phenylbutan-2-amine (2j): R_f = 0.48 (hexane/ethyl acetate 5/1); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42−7.21 (20 H, m), 4.70 (2 H, AB syst, *J* = 16.1), 4.00 (2 H, s), 3.83 (2 × 2 H, AB syst, *J* = 13.6), 3.82 (1 H, dd, *J* = 9.8, 3.1), 3.52 (1 H, dd, *J* = 13.4, 9.8), 3.09 (1 H, dd, *J* = 13.4, 3.1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.4, 139.8, 139.0, 129.1, 128.4, 127.8, 127.7, 127.2, 126.5, 126.2, 126.1, 64.5, 54.4, 53.6, 34.6, 27.9; IR (neat) 1662.

General Procedure for the Synthesis of Amino Aziridines 3. Method A. To a −15 °C stirred solution of the corresponding ketimine **2** (1 mmol) in THF (10 mL) was added $LiAlH_4$ (0.3 mL of solution 1.0 M in THF, 0.3 mmol). The resulting solution was stirred for 1 h, at the same temperature, and added to water. The resulting solution was filtered through a pad of Celite, and the filtrate was extracted with diethyl ether. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The amino aziridines **3** were examined by ^1H NMR to give the diastereomeric excess reported in Table 2. Flash column chromatography over silica gel (hexane/ethyl acetate = 15:1) provided pure compounds **3**.

Method B. To a stirred solution of the corresponding ketimine **2** (1 mmol) in methanol (10 mL) was added $NaBH_4$ (0.08 g, 2.0 mmol) at room temperature. After being stirred at the same temperature overnight, the mixture was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and extracted with diethyl ether. The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The amino aziridines **3** were examined by ^1H NMR to give the diastereomeric excess reported in Table 2. Flash column chromatography over silica gel (hexane/ethyl acetate = 15:1) provided pure compounds **3**.

When the reaction was carried out at −30 °C, the procedure was similar to that described above. After the mixture of aziridine and chloro diamine was isolated, MeLi (0.45 mL of solution 1.5 M in diethyl ether, 1 mmol) was added to a stirred solution of this mixture in THF (5 mL) at −78 °C. The resulting solution was stirred for 1 h at room temperature and quenched with a saturated aqueous solution of NH_4Cl (3 mL). Usual workup provided the amino aziridines **3**.

Method C. $NaBH_3CN$ (0.075 g, 1.2 mmol) was added to a stirred solution of **2** (1 mmol) in methanol (10 mL) at room temperature. After the solution was stirred overnight at the same temperature, the solvents were removed in vacuo. The resulting residue was dissolved in diethyl ether and washed with brine (5 mL). Usual workup provided the amino aziridine **3**, which was examined by ^1H NMR and/or GC/MS to give the diastereomeric excess reported in Table 3. Flash column chromatography (silica gel, hexane:ethyl acetate = 15:1) provided pure compound **3**.

(−)-(2*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)ethyl]aziridine (3a): R_f = 0.32 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D = -20.2$ (*c* 0.64, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.52−7.28 (10 H, m), 6.06 (1 H, ddt, *J* = 17.0, 10.0, 5.7), 5.29 (1 H, dd, *J* = 17.0, 1.7), 5.20 (1 H, dd, *J* = 10.0, 1.7), 3.83 (2 × 2 H, AB syst, *J* = 13.9), 3.02 (1 H, dd, *J* = 13.9, 6.1), 2.93−2.80 (2 H, m), 1.69−1.66 (2 H, m), 1.25 (1 H, d, *J* = 6.5), 1.07 (3 H, d, *J* = 7.0); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.4, 135.5, 128.3, 127.8, 126.3, 116.1, 63.4, 54.8, 53.9, 41.5, 30.1, 11.9; IR (neat) 3027, 1656; MS *m*/*z* 306 (M^+, <1), 224 (24), 215 (61), 91.0 (100); HRMS calcd for $C_{21}H_{26}N_2$ 306.2096, found 306.1953. Anal. Calcd for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55; N, 9.14. Found: C, 82.43; H, 8.47; N, 9.09. Chiral HPLC analysis: ee >99% (Chiralcel OD-H, UV detector 215 nm, 0.4 mL/min, 199/1 hexane/ethanol, t_R 10.6 min).

(−)-(2*S*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-1-propylaziridine (3b): R_f = 0.24 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D = -19.0$ (*c* 0.48, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.46−7.21 (10 H, m), 3.77 (2 × 2 H, AB syst, *J* = 13.4), 2.76 (1 H, dq, *J* = 7.0, 5.7), 2.30−2.15 (2 H, m), 1.66−1.53 (4 H, m), 1.15 (1 H, d, *J* = 7.0), 1.00 (3 H, d, *J* = 7.0), 0.98 (3 H, t, *J* = 7.4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.3, 128.3, 127.8, 126.4, 63.1, 54.6, 53.9, 41.6, 30.4, 22.7, 11.7; IR (neat) 3028; MS *m*/*z* 308 (M^+, <1), 224 (45), 217 (84), 91 (100); HRMS calcd for $C_{21}H_{28}N_2$ 308.2252, found 308.2247.

(−)-(2*S*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-1-cyclohexylaziridine (3c): R_f = 0.33 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −31.1 (*c* 0.74, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.51−7.25 (10 H, m), 3.82 (2 × 2 H, AB syst, *J* = 14.1), 2.91−2.78 (1 H, m), 2.00−1.05 (14 H, m), 1.03 (3 H, d, *J* = 6.9); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.4, 128.3, 127.8, 126.3, 69.3, 54.4, 53.8, 40.6, 33.0, 32.3, 28.9, 25.9, 24.7, 24.6, 11.3; IR (neat) 3027; HRMS calcd for $C_{24}H_{32}N_2$ 348.2565, found 348.2576.

(−)-(2*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)ethyl]aziridine (3d): R_f = 0.32 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −13.2 (*c* 0.74, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.55−7.32 (15 H, m), 3.75 (2 × 2 H, AB syst, *J* = 13.8), 3.56 (2 H, AB syst, *J* = 13.1), 2.80 (1 H, dt, *J* = 6.9, 6.7), 1.85 (1 H, ddd, *J* = 6.7, 6.4, 3.3), 1.72 (1 H, d, *J* = 3.3), 1.42 (1 H, d, *J* = 6.4), 1.14 (3 H, d, *J* = 6.9); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.4, 139.0, 128.3, 128.1, 127.9, 126.8, 126.3, 64.7, 54.9, 53.6, 41.4, 30.7, 12.7; IR (neat) 3027; MS, *m*/*z* 356 (M^+, <1), 265 (72), 224 (25), 91 (100); HRMS calcd for $C_{25}H_{28}N_2$ 356.2252, found 356.2239. Anal. Calcd for $C_{25}H_{28}N_2$: C, 84.23; H, 7.92; N, 7.86. Found: C, 84.12; H, 7.88; N, 7.79.

(+)-(2*S*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-1-(diphenylmethyl)aziridine (3e): R_f = 0.50 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = +3.3 (*c* 0.88, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.58−7.25 (20 H, m),3.56 (1 H, s), 3.52 (2 × 2 H, AB syst, *J* = 13.8), 2.78 (1 H, dq, *J* = 6.9, 5.9), 1.94 (1 H, ddd, *J* = 6.7, 5.9, 3.3), 1.82 (1 H, d, *J* = 3.3), 1.39 (1 H, d, *J* = 6.7), 1.05 (3 H, d, *J* = 6.9); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 143.5, 143.3, 140.6, 128.4, 128.2, 128.1, 128.0, 127.7, 127.1, 126.6, 126.2, 78.9, 54.3, 53.4, 41.9, 31.3, 12.7; IR (neat) 3026; MS *m*/*z* 432 (M^+, <1), 341 (M^+ − 91, 10), 224 (9), 167 (51), 91 (100); HRMS calcd for $C_{31}H_{32}N_2$ 432.2565, found 432.2562. Anal. Calcd for $C_{31}H_{32}N_2$: C, 86.07; H, 7.46; N, 6.48. Found: C, 86.18; H, 7.35; N, 6.40.

(−)-(2*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]aziridine (3f): R_f = 0.41 (hexane/ethyl acetate 10/1); $[\alpha]^{22}_D$ = −71.2 (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.45−7.19 (10 H, m), 6.11 (1 H, ddt, *J* = 18.2, 10.3, 6.2), 5.29 (1 H, dd, *J* = 18.2, 2.0), 5.23 (1 H, dd, *J* = 10.3, 2.0), 3.84 (2 × 2 H, AB syst, *J* = 13.3), 3.14 (1 H, dd, *J* = 13.6, 6.4), 2.87 (1 H, dd, *J* = 13.6, 5.9), 2.51−2.40 (1 H, m), 1.94−1.80 (1 H, m), 1.68−1.54 (1 H, m), 1.52−1.44 (1 H, m), 1.49 (1 H, d, *J* = 3.3), 1.21 (1 H, d, *J* = 6.4), 1.07−0.93 (1 H, m), 0.84 (3 H, d, *J* = 6.7), 0.51 (3 H, d, *J* = 6.7); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.5, 135.8, 128.9, 127.8, 126.4, 116.3, 63.5, 56.9, 53.9, 39.4, 38.9, 30.3, 24.0, 23.5, 21.3; IR (neat) 3028, 1656; MS *m*/*z* 348 (M^+, <1), 266 (14), 257 (27), 196 (58), 91 (100); HRMS calcd for $C_{24}H_{32}N_2$ 348.2565, found 348.2555.

(−)-(2*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]aziridine (3g): R_f = 0.42 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −52.5 (*c* 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ*7.60−7.30 (15 H, m), 3.70 (2 × 2 H, AB syst, *J* = 13.1), 3.61 (2 H, AB syst, *J* = 12.6), 2.50−2.43 (1 H, m), 2.00−1.91 (1 H, m), 1.81 (1 H, dt, *J* = 6.5, 3.5), 1.67−1.58 (1 H, m), 1.61 (1 H, d, *J* = 3.5), 1.40 (1 H, d, *J* = 6.5), 1.14−1.04 (1 H, m), 0.94 (3 H, d, *J* = 6.5), 0.57 (3 H, d, *J* = 6.5); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.5, 139.0, 128.9, 128.7, 128.2, 127.7, 127.0, 126.3, 64.8, 57.0, 53.5, 39.4, 39.3, 31.0, 23.9, 23.5, 21.2; IR (neat) 3028; MS *m*/*z* 398 (M^+, <1), 307 (62), 266 (39), 196 (82), 91 (100); HRMS calcd for $C_{28}H_{34}N_2$ 398.2722, found 398.2724. Anal. Calcd for $C_{28}H_{34}N_2$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.10; H, 8.66; N, 6.92.

(−)-(2*S*,1′*S*)-1-Cyclohexyl-2-[1′-(dibenzylamino)-2′-(phenyl)ethyl]aziridine (3h): R_f = 0.49 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −27.4 (*c* 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.28−7.04 (15 H, m), 3.93 (2 × 2 H, AB syst, *J* = 13.9), 2.93−2.69 (3 H, m), 2.07−1.19 (12 H, m), 1.33 (1 H, d, *J* = 3.3), 1.12 (1 H, d, *J* = 6.4); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.1, 129.3, 128.4, 127.8, 127.7, 126.3, 125.5, 69.4, 61.4, 53.6, 38.0, 35.7, 33.6, 32.4, 29.4, 26.0, 24.8, 24.6; IR (neat) 3026; HRMS calcd for $C_{30}H_{36}N_2$ 424.2878, found 424.2874. Anal. Calcd for $C_{30}H_{36}N_2$: C, 84.86; H, 8.55; N, 6.60. Found: C, 84.59; H, 8.50; N, 6.62.

(−)-(2*S*,1′*S*)-2-[1′-(Dibenzylamino)-2′-(phenyl)ethyl]-1-(*p*-methoxyphenyl)aziridine (3i): R_f = 0.40 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −75.6 (*c* 0.82, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.34−7.03 (19 H, m), 4.00 (2 × 2 H, AB syst, *J* = 13.7), 3.81 (3 H, s), 3.06−2.87 (2 H, m), 2.85−2.78 (1 H, m), 2.37 (1 H, dt, *J* = 6.6, 3.4), 1.86 (1 H, d, *J* = 6.6), 1.82 (1 H, d, *J* = 3.4); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 154.7, 148.2, 139.7, 129.3, 128.4, 127.9, 126.5, 125.7, 121.3, 114.1, 61.3, 55.4, 53.8, 39.5, 35.1, 31.7; IR (neat) 3026; HRMS calcd for $C_{31}H_{32}N_2O$ 448.2515, found 448.2511. Anal. Calcd for $C_{31}H_{32}N_2O$: C, 83.00; H, 7.19; N, 6.24. Found: C, 83.11; H, 7.10; N, 6.10.

(−)-(2*S*,1′*S*)1-Benzyl-2-[1′-(dibenzylamino)-2′-(phenyl)ethyl]aziridine (3j): R_f = 0.40 (hexane/ethyl acetate 5/1); $[\alpha]^{22}_D$ = −25.3 (*c* 0.82, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 7.53−7.04 (20 H, m), 3.76 (2 × 2 H, AB syst, *J* = 13.9), 3.57 (2 H, s), 3.04−2.91 (1 H, m), 2.84−2.70 (2 H, m), 1.86 (1 H, dt, *J* = 6.7, 3.6), 1.46 (1 H, d, *J* = 3.6), 1.33 (1 H, d, *J* = 6.7); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 140.1, 139.8, 139.0, 129.2, 128.6, 128.4, 128.2, 127.7, 127.0, 126.2, 125.5, 64.8, 61.4, 53.5, 39.2, 36.3, 31.3; IR (neat) 3026; MS, *m*/*z* 341 (M^+ − 91, 36), 300 (5), 196 (15), 91 (100); HRMS calcd for $C_{24}H_{25}N_2$ ($M - C_7H_7$)$^+$ 341.2018, found 341.2022.

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Supporting Information Available: ORTEP diagrams of **3e** and **3f**; X-ray crystallographic data, atomic coordinates, bond lengths and angles and torsional angles for structures **3e** and **3f**; and copies of the ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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