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Stereoselective Functionalization of 2-(1-Aminoalkyl)aziridines via Lithiation of Aziridine–Borane Complexes

José M. Concellón,* Pablo L. Bernad, and José Ramón Suárez[a]

Dedicated to Professor Joaquín Plumet on the occasion of his 60th birthday

Abstract: Highly selective functionalization of the aziridine ring of (2*S*,1′*S*)-2-(1′-aminoalkyl)aziridines **1**, through successive formation of aziridine–borane complexes, lithiation, treatment with a variety of electrophiles and final decomplexation is described. The influence of the structure of the starting complexes **2** and of the electrophiles in the stereoselectivity of this process has been studied. Finally, successive double lithiation–electrophile reactions were carried out affording enantiopure 1,2,3,3-tetrasubstituted aziridine–borane complexes with high selectivity.

Keywords: aziridines · deuteration · lithiation · regioselectivity

Introduction

The aziridine ring framework can be frequently found in natural and synthetic compounds of biological importance.[1] In addition, aziridines are versatile synthetic intermediates for the synthesis of many important compounds such as β-lactams[2] modified amino acids,[3] allylic amines[4] and nitrogen-containing functional compounds.[1a,g,h] The larger number of synthetic applications of aziridines are based on the strained heterocyclic ring by nucleophiles. In contrast, the chemistry of lithiated aziridines (aziridinyl anions) produced by direct lithiation/deprotonation has received much less attention.[5] Most diastereoselective lithiated aziridines have been generated from N-toluenesulfonyl aziridines[4c,6] or from aziridines bearing an anion stabilising group such as acyl,[7] alkenyl,[8] oxazolinyl,[9] benzotriazoyl,[10] sulfonyl[11] or trifluoromethyl[12] attached directly. Few methods to prepare aziridinyl anions without a stabilising substituent are known. The most important methods[13] are the Vedejs' lithiation of borane complexes of N-alkyl aziridines,[14] and the Beak lithiation of N-Boc aziridines.[15]

However, to the best of our knowledge, papers describing the synthesis of enantiopure aziridinyllithiums are scarce.[7,8b,c,9b,12,13b,14b,14c] Given these facts, a method to prepare polysubstituted enantiopure aziridines through highly diastereoselective lithiation would be interesting.

Recently, we described[16] a new methodology to obtain (1*R*,2*S*,1′*S*)-2-(1′-dibenzylaminoalkyl)aziridine(N^1-*B*)-boranes complexes **2** by a sequential treatment of (2*S*,1′*S*)-2-(1′-aminoalkyl)aziridines **1** with $BF_3{\cdot}Et_2O$ and reduction with $LiAlH_4$. The same boranes **2** were also obtained by direct reaction of **1** with borane. Interestingly, in both syntheses, complexation of borane took place in a stereospecific manner and only one diastereoisomer of complexes **2** was obtained enantiopure. In the same communication, we described two examples of selective lithiation of complexes **2** by using *sec*-BuLi.

Now, in this paper, we wish to extend these previous results. Thus, we describe the functionalization of the ring of aziridine of **1**, through successive formation of aziridine–borane complexes, lithiation with *sec*-BuLi, further treatment with a variety of electrophiles and final decomplexation using methanol. In this sense, we study the influence of the structure of the starting complexes **2** and of the electrophiles in the selectivity of this process. Finally, successive double lithiation–electrophile reactions were carried out affording enantiopure 1,2,3,3-tetrasubstituted aziridine–borane complexes with high selectivity.

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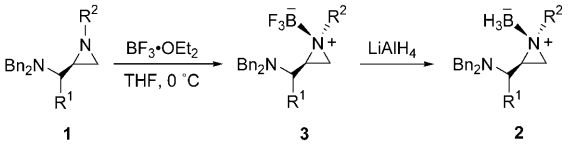
Results and Discussion

Synthesis of aziridine–borane complexes 2: The starting enantiopure aziridines **1** were prepared by reduction of α-amino ketimines derived from 1-aminoalkyl chloromethyl ketones, as reported.[17]

Compounds **1** were easily transformed into the corresponding aziridine–boranes complexes **2** by successive treatment with 1 equiv $BF_3{\cdot}Et_2O$ at 0 °C over 5 min and further reaction with 2 equiv $LiAlH_4$, at the same temperature, for 30 min (Scheme 1 and Table 1). Complexes **2** were obtained as sole product in high yield.



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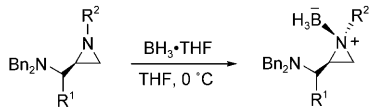
Scheme 1. Synthesis of aziridine–borane complexes **2** with $BF_3{\cdot}OEt_2$ and $LiAlH_4$.

Table 1. Synthesis of aminoalkylaziridine–borane complexes **2**.

	2	Method[a]	R^1	R^2	Yield [%][b]
1	**2a**	B	Me	propyl	79
2	**2b**	A	Me	allyl	76
3	**2b**	B	Me	allyl	80
4	**2c**	A	Me	Bn	71
5	**2c**	B	Me	Bn	74
6	**2d**	A	*i*Bu	allyl	75
7	**2e**	B	*i*Bu	cyclohexyl	80
8	**2f**	A	*i*Bu	Bn	81
9	**2f**	B	*i*Bu	Bn	77
10	**2g**	A	Bn	propyl	78
11	**2h**	A	Bn	cyclohexyl	77
12	**2i**	A	Bn	Bn	83
13	**2i**	B	Bn	Bn	82

[a] Method A: $BF_3{\cdot}OEt_2$ and $LiAlH_4$. Method B: $BH_3{\cdot}THF$. [b] Isolated yield after column chromatography based on the starting amino aziridine **1**.

The same borane complexes **2** can be also obtained by using a commercial borane/THF solution (Scheme 2 and Table 1).[1] Similar yields and purity of complexes **2** were obtained by using both methodologies (Table 1, entries 2–5, 8–9 and 12–13) and, consequently the cheaper $BF_3{\cdot}Et_2O$/$LiAlH_4$ methodology constitutes a valuable alternative to the use of BH_3/THF solution.



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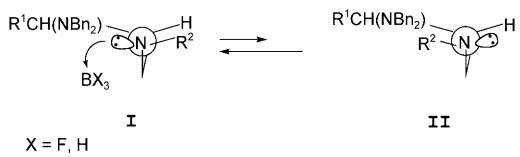
Scheme 2. Synthesis of aziridine–borane complexes **2** with $BF_3{\cdot}THF$.

Interestingly, only one diastereoisomer of **2** was obtained. The selectivity of the complexation reaction was established based on NMR analysis of the crude reaction mixture (^{1}H NMR: 300 MHz and ^{13}C NMR: 75 MHz) within the limits of the NMR assay. This process appears to be general; thus the reaction can be performed with a variety of amino aziridines derived from alanine, leucine, and phenylalanine and different amines (linear, cyclic and unsaturated). The level of diastereoisomeric purity of the borane–aziridine complexes **2** (>97 %) was not affected by the size of R^1 and R^2 in the starting amino aziridine. In contrast previous work involving reaction of tertiary amines with borane gave a mixture of diastereoisomers.[3]

Complexes **2** were surprisingly stable and could be purified by column chromatography and stored for several weeks at room temperature.

The structure and absolute configuration of compound **2f** was established based on its NOESY experiment and single-crystal X-ray analysis.[16] The configuration and structure of the other complexes **2** were assigned by analogy.

The described transformation and the observed stereochemistry of products **2** may be explained by assuming that the coordination of either Lewis acid ($BF_3{\cdot}Et_2O$) or BH_3 with aziridine nitrogen is favoured over the dibenzylamine nitrogen, due to steric hindrance. The isolation of complexes **2** as a single diastereoisomer can be explained by taking into account the difference in stability between the two diastereoisomers **I** and **II**, (Scheme 3). Conformer **I** predominates over **II** as a consequence of the steric hindrance involved, thus the reaction of **I** with $BF_3{\cdot}Et_2O$ or BH_3 is favoured.[4] To prove this fact, ^{1}H NMR experiments were carried out at variable temperature. The ^{1}H NMR spectrum of compound **1d** was studied over a temperature range from −80 °C to 120 °C. The spectra at temperature from −80 to 110 °C shows signals assigned to a single stereoisomer of compound **1d**. When the ^{1}H NMR spectrum of **1d** was recorded at 120 °C[18] a complex signals of olefinic protons was obtained. This multiplicity is according to the presence of



Scheme 3. Configurational equilibrium.

Abstract in Spanish: *Se describe la funcionalización altamente selectiva de (2S,1′S)-2-(1′-aminoalquil)aziridinas **1** a través de un proceso de formación de complejos borano–aziridina, litiación, tratamiento con electrófilos y descomplejación. También ha sido objeto de estudio la influencia de la estructura de los complejos **2** y de los electrófilos en el proceso. Finalmente, se ha llevado a cabo una doble reacción litiación y reacción con electrófilos dando lugar a complejos borano–aziridina 1,2,3,3-tetrasustituidas de forma enantiopura y con alta selectividad.*

the both possible conformers with a ratio of the two conformers about 9:1 (Figure 1).

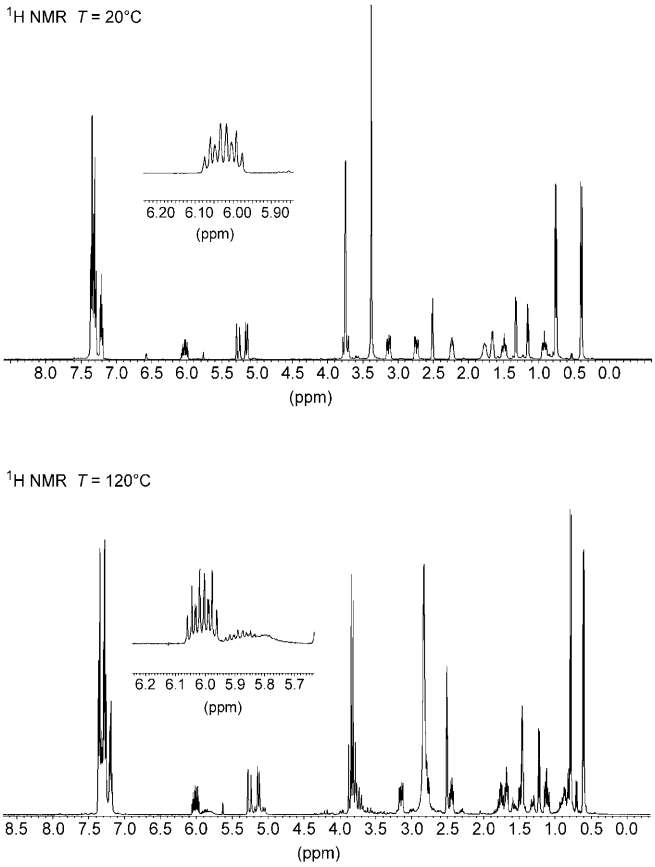
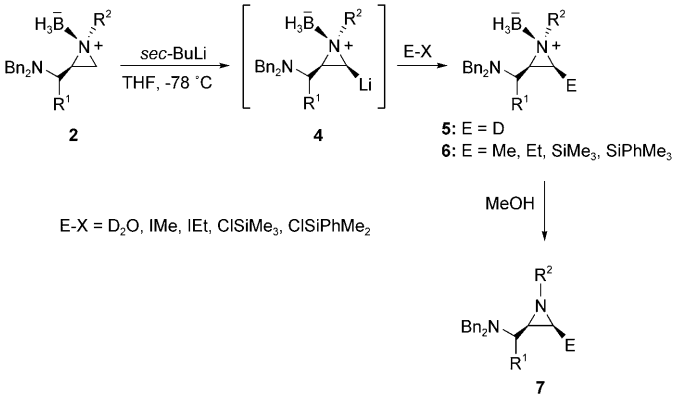


Figure 1. ^{1}H NMR studies at variable temperature of compound **1d** [D_6]DMSO.

Successive lithiation and reaction with electrophiles of aziridine–borane complexes 2: Treatment of a solution of complexes **2** in THF with *sec*-BuLi at −78 °C, over 45 min, gave a deep orange solution ascribed to the formation of lithiated aziridine–borane complexes **4**,[19] which was stable for 2 h at low temperature.[20]

Taking into account the usefulness of isotopically labelled compounds to establish the mechanism of organic reactions or the biosynthesis of many natural compounds,[21] we have paid particular attention to the deuteration of the aziridine ring. Thus, the trapping reaction of anions **4** with D_2O, furnished the corresponding 3-deuterioaziridine borane complexes **5** in good yields with total selectivity (^{1}H and ^{13}C NMR analysis) and with complete incorporation of deuterium (> 95 %, ^{1}H NMR) (Scheme 4 and Table 2).

As was to be expected, the amine–borane complex is the key to the lithiation of the aziridine ring. Indeed, it was found that the direct lithiation with *sec*-BuLi of aminoaziridine **1a** failed. No incorporation of deuterium was detected after successive treatment of **1a** with *sec*-BuLi and D_2O.



Scheme 4. Synthesis of functionalized borane complexes **5** and **6**.

Table 2. Synthesis of aminoalkylaziridine–borane Complexes deuterated **5**.

	5	R^1	R^2	*dr*	Yield [%][a]
1	**5aa**	Me	propyl	>97:3	93
2	**5ba**	Me	allyl	95:5	96
3	**5ca**	Me	Bn	>97:3	91
4	**5da**	*i*Bu	allyl	88:12	95
5	**5fa**	*i*Bu	Bn	79:21	91
6	**5ga**	Bn	propyl	>97:3	92
7	**5ia**	Bn	Bn	84:16	90

[a] Isolated yield after column chromatography based on the starting aziridine–borane complexes **2**.

The diastereoselectivity of the deuteration was determined by ^{1}H NMR spectra on the crude reaction products, showing that the diastereoselectivity was dependent on the structure of the starting aminoaziridine (Table 2). Thus, high or total stereoselectivity was obtained in all deuterations of the aminoaziridines derived from alanine (R^1 = Me) and in those derived from leucine (R^1 = *i*Bu) or phenylalanine (R^1 = Bn) with a R^2 group different to benzyl or allyl (Table 2). The stereoselectivity was lower (the diastereoisomer ratio ranged between 88:12 and 79:21) starting from aziridines with R^1 = *i*Bu or Bn and R^2 = Bn, or allyl (Table 2, entries 4, 5 and 7).

The configuration of the new stereogenic center generated in the deuteration was assigned based on disappearance or reduction of C_3-H signal *trans* to C_2-H in **5** which has the smaller vicinal *J* coupling constant (ranging between 6.4 and 5.0 Hz).

The reaction with other electrophiles such as iodoalkanes (MeI and EtI) or chlorotrialkylsilanes ($ClSiMe_3$ and $ClSiPhMe_2$) afforded trisubstituted aziridines **6** in good yields and with total regioselectivity (Table 3). In a similar manner to deuteration, there was very high or total stereoselectivity in the complexes derived from alanine, and from leucine, or phenylalanine with R^2 different to benzyl or allyl. Functionalization of aziridines derived from leucine or phenylalanine bearing a group benzyl or allyl on the aziridine ring, took place with lower stereoselectivity. No important differences in yield or diastereoselectivity were ob-

served when varying the electrophile (Table 3, entries 2–4, 5–6 and 7–8). The lower stereoselectivity observed in the alkylation and silylation of **6de** and **6ic** in comparison to their deuteration might be attributed to the increase of size of the electrophile.

Table 3. Synthesis of compound **6**.

	6	R^1	R^2	E	*dr*	Yield [%][a]
1	**6ab**	Me	propyl	$SiPhMe_2$	>97:3	77
2	**6bc**	Me	allyl	Me	>97:3	71
3	**6bd**	Me	allyl	Et	>97:3	73
4	**6be**	Me	allyl	$SiMe_3$	>97:3	73
5	**6cc**	Me	Bn	Me	>97:3	69
6	**6cd**	Me	Bn	Et	>97:3	75
7	**6de**	*i*Bu	allyl	$SiMe_3$	65:35	68
8	**6ec**	*i*Bu	C_6H_{11}	Me	>97:3	76
9	**6ee**	*i*Bu	C_6H_{11}	$SiMe_3$	>97:3	71
10	**6gc**	Bn	propyl	Me	>97:3	76
11	**6hb**	Bn	C_6H_{11}	$SiPhMe_2$	>97:3	72
12	**6ic**	Bn	Bn	Me	78:22[b]	67

[a] Isolated yield after column chromatography based on the starting aziridine–borane complexes **2**. [b] Major diastereoisomer can be isolated by column chromatography.

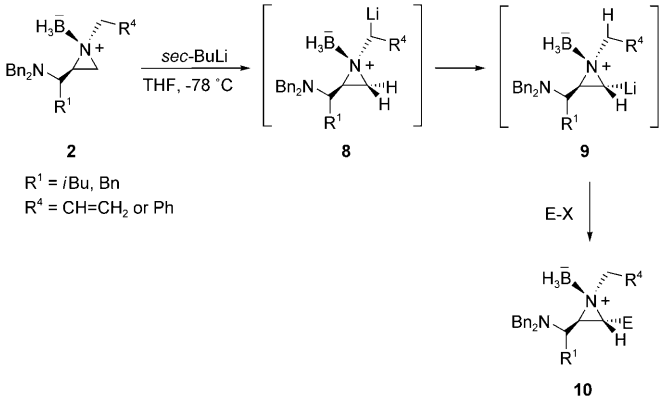
Attempts to capture lithioaziridine **4** with benzaldehyde or allyl bromide were unsuccessful.

Assuming retention of configuration from the C–Li intermediate through the C–D or C–E bond-forming step to obtain **5** or **6**, initial lithiation occurs mostly *syn* to boron, giving the aziridinium **4**. This *syn*-directing effect of N-BH_3 is in accordance with other lithiation of aziridine–borane complexes previously described.[14] This *syn* lithiation, with respect to boron atom, could also explain the stereoselectivity dependence on the structure of **2**. Thus, the decrease of stereoselectivity observed in the reactions of aminoaziridines derived from leucine (R^1 = *i*Bu) or phenylalanine (R^1 = Bn) with a group R^2 = benzyl or allyl, may be explained by assuming the increase in steric hindrance of R^1 could produce a competitive lithiation of the acidic hydrogen on the benzylic or allylic positions **8**(Scheme 5). In addition, the acidity of allyl or benzyl protons is increased by the activation produced by the borane–aziridine complex formation. Subsequent H–Li exchange from the benzylic or allylic position to the *anti* position with respect the boron on the aziridine ring **9** may explain the lower stereoselectivity observed in these cases. On the contrary, when there is not acidic protons in R^2, no competitive lithiation is produced and the lithiation takes place only in the aziridine ring (*syn* respect to the boron), affording the deuterated aziridine **5** or compounds **6** with very high or total stereoselectivity.

The 3-functionalized aziridine–borane complexes **5** and **6** were easily decomplexed by treatment with methanol, furnishing the corresponding enantiopure 3-functionalized 2-(1′-dibenzylaminoalkyl)aziridine **7** in excellent yield (> 92%, Table 4). Thus, the successive treatment of aminoaziridines with BH_3 or $BF_3{\cdot}Et_2O/LiAlH_4$, *sec*-BuLi, electrophiles and decomplexation constitutes an easy and effective methodology to enantioselective aziridine functionalization.

Double lithiation–electrophile reactions of aziridine–borane complexes 2a: The treatment of the deuterated aziridine–borane **5aa**, obtained as described above, with *sec*-BuLi at −78 °C during 45 min, afforded the aziridinyllithium **11**, in which the lithium is *anti* to the boron. This anion can be trapped with various electrophiles affording complexes **12** in which the ring is tetrasubstituted in high yield and with high stereoselectivity (Scheme 6 and Table 5). Hence, the successive lithiatio–deuteration and lithiation–alkylation or silylation of complex **2a** allowed the introduction of two different electrophiles in the aziridine ring.

The structure of compounds **12** was established based on the NOESY experiment of compound **12aae**[22] and on the comparison of the data of ^1H and ^{13}C NMR of compound **12** and **6**.



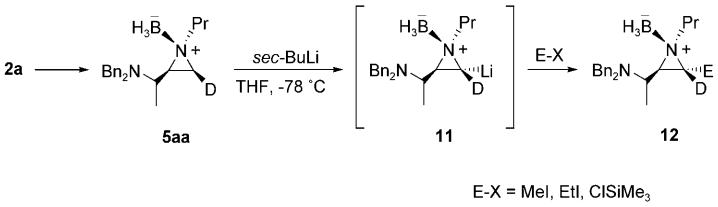
Scheme 5. Mechanism of lithiation of N-allyl or N-benzylaziridines.

Table 4. Decomplexation of **5** and **6**.

	7	R^1	R^2	E	Yield [%][a]
1	**7bc**	Me	allyl	Me	92
2	**7bd**	Me	allyl	Et	94
3	**7be**	Me	allyl	$SiMe_3$	93
4	**7da**	*i*Bu	allyl	D	94
5	**7ic**	Bn	Bn	Me	92[b]

[a] Isolated yield after column chromatography based on the starting aziridine–borane complexes **4** or **5**. [b] Referred only to major diastereoisomer.

The different stereochemistry observed in the lithiation reaction (*anti* versus *syn* to the boron) can be explained by taking into account the isotopic effect. It is difficult to abstract the deuterium atom in comparison to the lithiation of the C–H bond. Hence, in these cases the *syn*-directing effect



Scheme 6. Double lithiation of aziridine–borane complexes **2a**.

Table 5. Double lithiation of aziridine–borane complexes **2a**.

	12	E	*dr*	Yield [%][a]
1	**12aac**	Me	>97:3	77
2	**12aad**	Et	>97:3	71
3	**12aae**	$SiMe_3$	>97:3	73

[a] Isolated yield after column chromatography based on the starting aziridine–borane complex **5aa**.

of N-BH_3 was insufficient to produce the lithiation of C–D instead of the weaker C–H bond.

The order of the introduction of electrophiles is crucial. When compounds **6** (alkylated or silylated complexes) were lithiated with *sec*-BuLi and later treated with electrophiles (including D_2O), no second functionalization of the aziridine ring took place, and the starting complex **6** was recovered. On this basis, we must conclude that the second lithiation reaction and/or subsequent electrophile reaction is strongly influenced by steric factors.

Conclusion

We have described a easy methodology to easily prepare enantiopure 2-(1-aminoalkyl)aziridine–borane complexes **2** by reaction of the starting aminoaziridines with $BF_3{\cdot}Et_2O$ followed by reduction with $LiAlH_4$. This method is cheaper than the classical direct reaction with BH_3/THF solution. The lithiation of these complexes with *sec*-BuLi, followed by reaction with electrophiles takes place in high yield and with total regioselectivity. The stereoselectivity was dependent on the structure of the starting aminoaziridine. So, regio- and stereoselective C-3 functionalization of 2-(1-aminoalkyl)aziridine **1** can be effected by successive deprotonation/electrophile/decomplexation reactions of the corresponding borane complex **2**. Finally, both C^2-deuteration and C^2-alkylation or silylation of aziridine–borane complexes **2** can be carried out in good yield and with high selectivity by successive lithiation–deuteration and lithiation–alkylation or silylation of complexes **2**.

Experimental Section

General methods: All reactions were carried out under an atmosphere of dry N_2 using oven-dried glassware and syringes. THF was distilled from sodium/benzophenone immediately prior to use. All reagents were purchased in the higher quality available and were used without further purification. $BF_3{\cdot}OEt_2$ was distilled from CaH_2 and stored over activated 4 Å molecular sieves. The solvents used in column chromatography, hexane, EtOAc, were obtained from commercial suppliers and used without further distillation. TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on silica gel 60, 230–240 mesh. ^{1}H NMR (200, 300, 400 MHz) and ^{13}C NMR (50, 75, 100 MHz) spectra were measured at room temperature on a Bruker AC-200, AC-300 and AMX-400 instruments, respectively, with tetramethylsilane ($\delta=0.0$, ^{1}H NMR) or $CDCl_3$ ($\delta=77.00$, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 5987 A, and the intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT 95 spectrometer. Elemental analyses were carried out on a Perkin–Elmer 2400 and Carlo Erba 1108 microanalyzers.

Synthesis of aziridine–borane complexes 2: *Method A*: $BF_3{\cdot}OEt_2$ (0.025 mL, 0.2 mmol) and $LiAlH_4$ (0.4 mL, 0.4 mmol, 1 M in THF) were successively added at 0 °C to a stirred solution of the corresponding aminoaziridine **1** (0.2 mmol) in THF (2 mL). After stirring at this temperature for 30 min, the reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and the mixture was stirred at room temperature for 5 min. Then, the aqueous phase was extracted with Et_2O (3×5 mL), and the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo afforded the crude complexes **2**, which were purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). Yields are given in Table 1.

Method B: BH_3/THF (0.22 mL, 0.22 mmol, 1 M in THF) was added at 0 °C to a stirred solution of the corresponding aminoaziridine **1** (0.2 mmol) in THF (2 mL). After stirring at this temperature for 30 min, the reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL). The workup was similar to that in Method A.

(1*R*,2*S*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-1-propylaziridine(*N*^{1}-*B*)-borane (2a): Colorless oil; $R_f=0.47$ (hexane/EtOAc 3:1); $[\alpha]_D^{25}=-0.7$ ($c=1.06$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.52$–7.16 (m, 10H), 3.86 (AB syst., $J=14.0$ Hz, 4H), 3.65 (apparent qt, $J=7.3$ Hz, 1H), 2.67 (td, $J=11.7$, 5.4 Hz, 1H), 2.38–2.21 (m, 3H), 2.01 (d, $J=7.2$ Hz, 2H), 1.92–1.79 (m, 1H), 1.34 (brs, 3H), 1.16 (d, $J=6.9$ Hz, 3H), 0.93 (d, $J=7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.8$ (2×C), 128.7 (4×CH), 128.0 (4×CH), 126.7 (2×CH), 66.7 (CH_2), 54.4 (2×CH_2), 52.7 (CH), 50.8 (CH), 40.3 (CH_2), 19.6 (CH_2), 13.5 (CH_3), 11.1 (CH_3); MS (70 eV, EI): *m*/*z* (%): 321 (4) [M^+–H], 224 (53), 217 (82), 196 (59), 146 (40), 91 (100); IR (neat): $\tilde{\nu}=3028$, 2385, 2251, 1494, 1454 cm^{-1}; HRMS (70 eV): *m*/*z*: calcd for $C_{21}H_{30}BN_2$: 321.2497, found 321.2512 [M^+–H]; elemental analysis calcd (%) for $C_{21}H_{31}BN_2$: C 78.26, H 9.69, N 8.69; found: C 78.39, H 9.51, N 8.75.

(1*R*,2*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)ethyl]aziridine(*N*^{1}-*B*)-borane (2b): Colorless oil; $[\alpha]_D^{25}=-13.3$ ($c=0.51$, $CHCl_3$); $R_f=0.51$ (hexane/EtOAc 3:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=7.48$–7.20 (m, 10H), 6.18–6.00 (m, 1H), 5.33–5.14 (m, 2H), 3.80 (AB syst., $J=14.1$ Hz, 4H), 3.64 (apparent qt, $J=7.2$ Hz, 1H), 3.27 (dd, $J=13.1$, 6.4 Hz, 1H), 3.13 (dd, $J=13.1$, 7.1 Hz, 1H), 2.29 (apparent q, $J=8.0$ Hz, 1H), 2.07 (dd, $J=8.0$, 1.5 Hz, 1H), 1.95 (dd, $J=6.4$, 1.5 Hz, 1 H), 1.29 (brs, 3H), 1.13 (d, $J=6.9$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=140.0$ (2×C), 130.8 (CH), 128.7 (4×CH), 128.1 (4×CH), 126.8 (2×CH), 121.1 (CH_2), 66.1 (CH_2), 54.4 (2×CH_2), 53.2 (CH), 49.5 (CH), 38.8 (CH_2), 13.7 (CH_3); IR (neat): $\tilde{\nu}=3424$, 3027, 2386, 2250, 1494, 1454 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{29}BN_2$: C 78.75, H 9.13, N 8.75; found: C 78.89, H 9.21, N 8.65.

(1*R*,2*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)ethyl]aziridine(*N*^{1}-*B*)-borane (2c): White solid; $R_f=0.49$ (hexane/EtOAc 3:1); m.p. 84–86 °C; $[\alpha]_D^{25}=-10.7$ ($c=1.16$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.48$–7.29 (m, 15H), 4.16 (d, $J=13.2$ Hz, 1H), 3.89 (d, $J=13.2$ Hz, 1H), 3.86 (AB syst., $J=14.4$ Hz, 4H), 3.68 (apparent t, $J=7.0$ Hz, 1H), 2.42 (apparent q, $J=7.5$ Hz, 1H), 2.13 (d, $J=8.2$ Hz, 1H), 2.04 (dd, $J=6.4$, 1.6 Hz, 1H), 1.31 (brs, 3H), 1.14 (d, $J=7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.8$ (2×C), 131.9 (C), 131.4, 128.9, 128.6, 128.4, 128.0, 126.7 (15×CH), 65.2 (CH_2), 54.2 (2×CH_2), 52.4 (CH), 46.9 (CH), 38.0 (CH_2), 14.1 (CH_3);

MS (70 eV, EI): *m/z* (%): 370 (<1) [M^+], 265 (58), 224 (18), 196 (30), 146 (17), 91 (100); IR (neat): 3027, 2930, 2385, 2283, 1495, 1454 cm^{-1}; HRMS (70 eV): *m/z*: calcd for $C_{25}H_{31}BN_2$: 370.2580, found 370.2584 [M^+]; elemental analysis calcd (%) for $C_{25}H_{31}BN_2$: C 81.08, H 8.44, N 7.56; found: C 81.22, H 8.52, N 7.45.

(1*R*,2*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]aziridine(*N*^{1}-*B*)-borane (2d): White solid; R_f=0.50 (hexane/EtOAc 3:1); m.p. 79–81 °C; $[\alpha]_D^{25}$ = −28.9 (*c* = 0.47, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.21 (m, 10H), 6.27–6.13 (m, 1H), 5.39 (d, *J*=10.2 Hz, 1H), 5.28 (d, *J*=17.2 Hz, 1H), 3.83 (AB syst., *J*=8.9 Hz, 4H), 3.51–3.41 (m, 2H), 3.20 (dd, *J*=13.1, 7.5 Hz, 1H), 2.38 (apparent q, *J*=8.1 Hz, 1H), 2.14 (d, *J*=8.3 Hz, 1H), 2.01 (d, *J*=5.0 Hz, 1H), 1.89–1.78 (m, 1H), 1.69–1.60 (m, 1H), 1.30 (brs, 3H), 1.15–1.06 (m, 1H), 0.89 (d, *J*=6.7 Hz, 3H), 0.64 (d, *J*=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1 (2×C), 130.9 (CH), 129.2 (4×CH), 127.9 (4×CH), 126.7 (2×CH), 121.7 (CH_2), 66.3 (CH_2), 54.8 (CH), 54.1 (2×CH_2), 47.8 (CH), 40.1 (CH_2), 39.1 (CH_2), 24.5 (CH), 23.2 (CH_3), 21.7 (CH_3); MS (70 eV, EI): *m/z* (%): 361 (<1) [M^+−H], 266 (44), 257 (56), 196 (84), 91 (100); IR (neat): 3426, 3029, 2956, 2929, 2384, 2282, 1494, 1454 cm^{-1}; HRMS (70 eV): *m/z*: calcd for $C_{24}H_{34}BN_2$: 361.2810, found 361.2819 [M^+−H]; elemental analysis calcd (%) for $C_{24}H_{35}BN_2$: C 79.55, H 9.74, N 7.73; found: C 79.70, H 9.63, N 7.56.

(1*R*,2*S*,1′*S*)-1-Cyclohexyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]aziridine-(*N*^{1}-*B*)-borane (2e): White solid; R_f=0.45 (hexane/EtOAc 3:1); m.p. 83–84 °C; $[\alpha]_D^{25}$ = −24.8 (*c* = 1.60, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45–7.23 (m, 10H), 3.87 (AB syst., *J*=16.9 Hz, 4H), 3.71–3.58 (m, 1H), 2.28 (apparent q, *J*=6.7 Hz, 1H), 2.06–1.82 (m, 10H), 1.74–1.60 (m, 4H), 1.34–0.97 (m, 5H), 0.87 (d, *J*=6.1 Hz, 3H), 0.59 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.0 (2×C), 129.2 (4×CH), 127.9 (4×CH), 126.7 (2×CH), 74.3 (CH), 53.9 (2×CH_2), 53.6 (CH), 49.8 (CH), 40.7 (CH_2), 39.8 (CH_2), 29.7 (CH_2), 29.2 (CH_2), 25.5 (2×CH_2), 25.4 (CH_2), 24.4 (CH), 23.4 (CH_3), 21.3 (CH_3); IR (neat): $\tilde{\nu}$=3029, 2931, 2856, 2378, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 403 (<1) [M^+−H], 299 (37), 266 (86), 194 (35), 91 (100); HRMS (70 eV): *m/z*: calcd for $C_{27}H_{40}BN_2$: 403.3279, found 403.3286 [M^+−H]; elemental analysis calcd (%) for $C_{27}H_{41}BN_2$: C 80.18, H 10.22, N 6.93; found: C 79.98, H 10.31, N 6.84.

(1*R*,2*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]aziridine-(*N*^{1}-*B*)-borane (2f): White solid; R_f=0.53 (hexane/EtOAc 3:1); m.p. 81–83 °C; $[\alpha]_D^{25}$ = −21.0 (*c* = 0.92, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.48–7.22 (m, 15H), 4.30 (d, *J*=13.6 Hz, 1H), 3.86 (d, *J*=13.6 Hz, 1H), 3.61 (AB syst., *J*=13.6 Hz, 4H), 2.43 (apparent q, *J*=7.2 Hz, 1H), 2.18 (d, *J*=8.7 Hz, 1H), 2.07 (d, *J*=6.4 Hz, 1H), 1.82–1.71 (m, 1H), 1.64–1.50 (m, 1H), 1.31 (brs, 3H), 1.08–0.93 (m, 2H), 0.85 (d, *J*=6.7 Hz, 3H), 0.58 (d, *J*=6.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.0 (3×C), 131.8, 129.1, 128.5, 127.9, 126.7 (15×CH), 65.5 (CH_2), 54.3 (CH), 53.8 (2×CH_2), 44.6 (CH), 40.4 (CH_2), 38.8 (CH_2), 24.4 (CH), 23.3 (CH_3), 21.4 (CH_3); IR (neat): $\tilde{\nu}$ = 3426, 3028, 2385, 2281, 1494, 1454 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{37}BN_2$: C 81.54, H 9.04, N 6.79; found: C 81.63, H 9.12, N 6.65.

(1*R*,2*S*,1′*S*)-2-[1′-(Dibenzylamino)-2′-(phenyl)ethyl]-1-propylaziridine-(*N*^{1}-*B*)-borane (2g): White solid; R_f=0.51 (hexane/EtOAc 3:1); m.p. 88–90 °C; $[\alpha]_D^{25}$ = −23.7 (*c* = 2.70, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.12 (m, 15H), 3.98 (AB syst., *J*=14.1 Hz, 4H), 3.87–3.78 (m, 1H), 3.07 (dd, *J*=13.5, 6.2 Hz, 1H), 2.79 (dd, *J*=13.5, 9.1 Hz, 1H), 2.46 (apparent t, *J*=8.0 Hz, 2H), 2.26 (apparent q, *J*=8.0 Hz, 1H), 1.92–1.88 (m, 2H), 1.80 (d, *J*=7.3 Hz, 1H), 1.48 (d, *J*=5.2 Hz, 1H), 1.35 (brs, 3H), 0.92 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.3 (2×C), 138.7 (C), 128.9 (2×CH), 128.7 (4×CH), 128.0 (2×CH), 127.8 (4×CH), 126.6 (2×CH), 125.9 (CH), 66.2 (CH_2), 59.4 (CH), 54.1 (2×CH_2), 48.3 (CH), 40.3 (CH_2), 36.0 (CH_2), 19.4 (CH_2), 11.0 (CH_3); IR (neat): $\tilde{\nu}$= 3246, 3028, 2933, 2360, 1601, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 397 (<1) [M^+−H], 293 (16), 196 (12), 106 (14), 91 (100), 65 (15); HRMS (70 eV): *m/z*: calcd for $C_{27}H_{34}BN_2$: 397.2810, found 397.2814 [M^+−H]; elemental analysis calcd (%) for $C_{27}H_{35}BN_2$: C 81.40, H 8.86, N 7.03; found: C 81.56, H 8.96, N 6.89.

(1*R*,2*S*,1′*S*)-1-Cyclohexyl-2-[1′-(dibenzylamino)-2′-(phenyl)ethyl]aziridine-(*N*^{1}-*B*)-borane (2h): White solid; R_f=0.51 (hexane/EtOAc 3:1); m.p. 84–86 °C; $[\alpha]_D^{25}$ = −45.1 (*c* = 1.77, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.42–7.09 (m, 15H), 3.97 (AB syst., *J*=13.9 Hz, 4H), 3.04 (dd, *J*=13.6, 6.9 Hz, 1H), 2.78 (dd, *J*=13.6, 8.7 Hz, 1H), 2.23 (apparent q, *J*=8.2 Hz, 1H), 2.11–1.56 (m, 9H), 1.54–1.15 (m, 6H), 1.00–0.93 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.3 (2×C), 138.9 (C), 129.2 (2×CH), 128.9 (4×CH), 128.1 (2×CH), 127.9 (4×CH), 126.7 (2×CH), 126.0 (CH), 73.9 (CH), 57.9 (CH), 54.0 (2×CH_2), 49.2 (CH), 40.1 (CH_2), 36.7 (CH_2), 29.6 (CH_2), 29.0 (CH_2), 25.4 (2×CH_2), 25.3 (CH_2); IR (neat): $\tilde{\nu}$ = 3026, 2385, 2251, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 437 (<2) [M^+−H], 300 (29), 208 (24), 91 (100), 65 (26); HRMS (70 eV): *m/z*: calcd for $C_{30}H_{38}BN_2$: 473.3125, found 473.3141 [M^+−H]; elemental analysis calcd (%) for $C_{30}H_{39}BN_2$: C 82.18, H 8.97, N 6.39; found: C 82.34, H 8.88, N 6.32.

(1*R*,2*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-2′-(phenyl)ethyl]aziridine(*N*^{1}-*B*)-borane (2i): White solid; R_f=0.56 (hexane/EtOAc 3:1); m.p. 82–85 °C; $[\alpha]_D^{25}$ = −17.1 (*c* = 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.06 (m, 20H), 4.09–3.78 (m, 7H), 3.03 (dd, *J*=13.6, 6.4 Hz, 1H), 2.74 (dd, *J*=13.6, 5.0 Hz, 1H), 2.40 (apparent q, *J*=8.1 Hz, 1H), 1.95 (d, *J*=6.9 Hz, 1H), 1.58 (d, *J*=6.2 Hz, 1H), 1.37 (brs, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5 (2×C), 138.7 (C), 131.7 (C), 131.5, 129.1, 129.0, 128.7, 128.4, 128.1, 128.0, 126.7, 126.0 (20×CH), 65.0 (CH_2), 59.0 (CH), 54.0 (2×CH_2), 44.5 (CH), 38.2 (CH_2), 36.6 (CH_2); IR (neat): $\tilde{\nu}$ = 3426, 3061, 3027, 2383, 2283, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 341 (75) [M^+−$C_7H_{10}B$], 250 (34), 92 (40), 91 (100), 65 (45); HRMS (70 eV): *m/z*: calcd for $C_{24}H_{35}N_2$: 341.2012, found 341.2022 [M^+−$C_7H_{10}B$]; elemental analysis calcd (%) for $C_{31}H_{35}BN_2$: C 83.40, H 7.90, N 6.27; found: C 83.61, H 7.79, N 6.33.

Synthesis of compounds 5 and 6: A solution of *sec*-BuLi (0.54 mL, 1.4 M in cyclohexane) was added at −78 °C to a stirred solution of the corresponding aziridine–borane complexes **2** (0.15 mmol) in THF (1 mL). After 45 min at this temperature, the corresponding electrophile was added (5.5 equiv) and the mixture was stirred during 30 min at −78 °C. Then the reaction was quenched with a saturated aqueous solution of NH_4Cl (5 mL) and the mixture was stirred at room temperature for 5 min. The aqueous phase was extracted with Et_2O (3×5 mL), and the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo afforded the crude complexes **5** or **6**, which were purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). Yields are given in Tables 2 and 3.

Treatment of **5** or **6** (0.10 mmol) with MeOH (1 mL) at room temperature during 24 h gave compounds **7**.

(1*R*,2*S*,3*S*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-3-deuterio-1-propyl aziridine-(*N*^{1}-*B*)-borane (5aa): Colorless oil; R_f=0.47 (hexane/EtOAc 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.26 (m, 10H), 4.17 (AB syst., *J*= 14.1 Hz, 4H), 3.68–3.58 (m, 1H), 2.64 (ddd, *J*=17.0, 11.6, 5.4 Hz, 1H), 2.33–2.19 (m, 2H), 1.99–1.77 (m, 3H), 1.33 (brs, 3H), 1.14 (d, *J*=6.9 Hz, 3H), 0.91 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (2×C), 128.7 (4×CH), 128.0 (4×CH), 126.7 (2×CH), 66.7 (CH_2), 54.4 (2×CH_2), 52.7 (CH), 50.7 (CH), 40.0 (CHD, t, *J*=25.5 Hz), 19.6 (CH_2), 13.5 (CH_3), 11.1 (CH_3); IR (neat): $\tilde{\nu}$ = 3028, 2384, 2251, 1494, 1454 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{30}DBN_2$: C 78.02, H 9.98, N 8.66; found: C 78.18, H 9.88, N 8.74.

(1*R*,2*S*,3*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)ethyl]-3-deuterioaziridine-(*N*^{1}-*B*)-borane (5ba): Data on the 95:5 mixture of diastereoisomers: Colorless oil; R_f=0.50 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −13.1 (*c* = 0.62, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.20 (m, 10H), 6.13–5.99 (m, 1H), 5.32–5.15 (m, 2H), 3.79 (AB syst., *J*=14.1 Hz, 4H), 3.59 (apparent qt, *J*=6.9 Hz, 1H), 3.27 (dd, *J*=13.1, 6.6 Hz, 1H), 3.13 (dd, *J*=13.1, 7.3 Hz, 1H), 2.27 (apparent t, *J*=7.9 Hz, 1H), 2.05 (d, *J*=8.5 Hz, 1H, major isomer), 1.94 (dd, *J*=6.4 Hz, 1H, minor isomer), 1.28 (brs, 3H), 1.12 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0 (2×C), 130.8 (CH), 128.7 (4×CH), 128.1 (4×CH), 126.8 (2×CH), 121.5 (CH_2), 66.1 (CH_2), 54.4 (2×CH_2), 53.1 (CH), 49.4 (CH), 38.5 (CHD, t, *J*= 24.3 Hz), 13.7 (CH_3); IR (neat): $\tilde{\nu}$ = 3424, 3028, 2385, 2250, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 361 (2) [M^+−H], 224 (26), 216 (47), 146 (22), 91 (100); HRMS (70 eV): *m/z*: calcd for $C_{21}H_{27}DBN_2$: 320.2403, found 320.2407 [M^+−H]; elemental analysis calcd (%) for $C_{21}H_{28}DBN_2$: C 78.50, H 9.41, N 8.72; found: C 78.63, H 9.50, N 8.64.

(1*R*,2*S*,3*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)ethyl]-3-deuterio-aziridine-(N^1-*B*)-borane (5ca): Colorless oil; R_f=0.49 (hexane/EtOAc 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.11 (m, 15H), 4.11 (d, J= 13.2 Hz, 1H), 3.85 (d, J=13.2 Hz, 1H), 3.71 (AB syst., J=14.6 Hz, 4H), 3.69–3.64 (m, 1H), 2.37 (apparent t, J=7.7 Hz, 1H), 2.08 (d, J=8.1 Hz, 1H), 1.32 (brs, 3H), 1.09 (d, J=6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9 (2×C), 131.9 (C), 131.4 (2×CH), 128.9 (CH), 128.6 (4×CH), 128.4 (2×CH), 128.0 (4×CH), 126.7 (2×CH), 65.2 (CH_2), 54.2 (2×CH_2), 52.4 (CH), 46.9 (CH), 37.7 (CHD, t, J=26.6 Hz), 14.2 (CH_3); IR (neat): $\tilde{\nu}$ = 3026, 2930, 2383, 2281, 1495, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 370 (<1) [M^+−H], 266 (81), 224 (507), 196 (66), 146 (49), 91 (100); HRMS (70 eV): m/z: calcd for $C_{25}H_{29}DBN_2$: 370.2559, found 370.2552 [M^+−H].

(1*R*,2*S*,3*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]-3-deuterioaziridine(N^1-*B*)-borane (5da): Data on the 88:12 mixture of diastereoisomers: colorless oil; R_f=0.51 (hexane/EtOAc 3:1); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.43–7.20 (m, 10H), 6.24–6.01 (m, 1H), 5.39–5.20 (m, 2H), 3.81 (AB syst., J=8.4 Hz, 4H), 3.47–3.40 (m, 2H), 3.18 (dd, J=13.1, 7.2 Hz, 1H), 2.35 (apparent t, J=8.0 Hz, 1H), 2.10 (d, J= 8.2 Hz, 1H, major isomer), 1.98 (d, J=5.1 Hz, 1H, minor isomer), 1.80–1.54 (m, 2H), 1.29 (brs, 3H), 1.15–1.01 (m, 1H), 0.86 (d, J=6.4 Hz, 3H), 0.61 (d, J=6.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.1 (2×C), 130.9 (CH), 129.2 (4×CH), 127.9 (4×CH), 126.7 (2×CH), 121.7 (CH_2), 66.3 (CH), 54.8 (CH), 54.2 (2×CH_2), 47.7 (CH), 40.2 (CH_2), 38.7 (CHD, t, J=25.3 Hz), 24.5 (CH), 23.2 (CH_3), 21.7 (CH_3); IR (neat): $\tilde{\nu}$ = 3427, 3029, 2955, 2929, 2385, 1495, 1454 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{34}DBN_2$: C 79.33, H 9.99, N 7.71; found: C 79.50, H 9.88, N 7.77.

(1*R*,2*S*,3*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]-3-deuterioaziridine(N^1-*B*)-borane (5fa): Data on the 79:21 mixture of diastereoisomers: colorless oil; R_f=0.52 (hexane/EtOAc 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.23 (m, 15H), 4.32 (d, J=13.1 Hz, 1H), 3.88 (d, J=13.1 Hz, 1H), 3.64 (AB syst., J=13.7 Hz, 4H), 3.54–3.47 (m, 1H), 2.45 (apparent t, J=8.2 Hz, 1H), 2.20 (d, J=8.3 Hz, 1H, major isomer), 2.08 (d, J=6.6 Hz, 1H, minor isomer), 1.86–1.80 (m, 1H), 1.65–1.55 (m, 1H), 1.33 (brs, 3H), 1.09–1.00 (m, 1H), 0.88 (d, J=6.6 Hz, 3H), 0.61 (d, J=6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0 (2×C), 131.8 (2×CH and C), 129.1 (5×CH), 128.5 (2×CH), 127.9 (4×CH), 126.7 (2×CH), 65.4 (CH_2), 54.2 (CH), 53.8 (2×CH_2), 44.5 (CH), 40.4 (CH_2), 38.4 (CHD, t, J=27.4 Hz), 24.3 (CH), 23.3 (CH_3), 21.4 (CH_3); IR (neat): $\tilde{\nu}$ = 3426, 3029, 2384, 2281, 1495, 1454 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{36}DBN_2$: C 81.34, H 9.26, N 6.78; found: C 81.49, H 9.12, N 6.85.

(1*R*,2*S*,3*S*,1′*S*)-2-[1′-(Dibenzylamino)-2′-(phenyl)ethyl]-3-deuterio-1-propylaziridine(N^1-*B*)-borane (5ga): White solid; R_f=0.50 (hexane/EtOAc 3:1); m.p. 89–92 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.46–7.08 (m, 15H), 3.96 (AB syst., J=14.4 Hz, 4H), 3.86–3.74 (m, 1H), 3.06 (dd, J=13.6, 6.2 Hz, 1H), 2.76 (dd, J=13.6, 9.2 Hz, 1H), 2.48–2.38 (m, 2H), 2.21 (apparent t, J=8.5 Hz, 1H), 1.87 (apparent q, J=7.9 Hz, 2H), 1.77 (d, J=7.3 Hz, 1H), 1.33 (brs, 3H), 0.89 (t, J=7.5 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.5 (2×C), 138.7 (C), 129.1 (2×CH), 128.9 (4×CH), 128.2 (2×CH), 128.0 (4×CH), 126.8 (2×CH), 126.1 (CH), 66.5 (CH_2), 59.8 (CH), 54.4 (2×CH_2), 48.6 (CH), 40.1 (CHD, t, J=26.4 Hz), 36.2 (CH_2), 19.5 (CH_2), 11.2 (CH_3); MS (70 eV, EI): m/z (%): 398 (2) [M^+−H], 294 (19), 203 (11), 174 (12), 91 (100), 65 (14); IR (neat): $\tilde{\nu}$ = 3027, 2970, 2365, 1601, 1494, 1454 cm^{-1}; HRMS (70 eV): m/z: calcd for $C_{27}H_{34}DBN_2$: 398.2872, found 398.2870 [M^+−H]; elemental analysis calcd (%) for $C_{27}H_{34}DBN_2$: C 81.19, H 9.08, N 7.01; found: C 81.33, H 8.95, N 6.87.

(1*R*,2*S*,3*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-2′-(phenyl)ethyl]-3-deuterioaziridine(N^1-*B*)-borane (5ia): Data on the 84:16 mixture of diastereoisomers: colorless oil; R_f=0.54 (hexane/EtOAc 3:1); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.43–7.00 (m, 20H), 3.97 (AB syst., J=13.1 Hz, 2H), 3.96–3.82 (m, 1H), 3.81 (AB syst., J=14.4 Hz, 4H), 3.00 (dd, J= 13.6, 6.4 Hz, 1H), 2.70 (dd, J=13.6, 8.7 Hz, 1H), 2.36 (apparent t, J= 8.2 Hz, 1H), 1.90 (d, J=8.2 Hz, 1H, major isomer), 1.53 (d, J=6.4 Hz, 1H, minor isomer), 1.34 (brs, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.6 (2×C), 138.7 (C), 131.7 (C), 131.6, 129.1, 129.0, 128.8, 128.4, 128.2, 128.0, 126.8, 126.1 (20×CH), 65.0 (CH_2), 59.1 (CH), 54.1 (2×CH_2), 44.5 (CH), 37.8 (CHD, t, J=25.3 Hz), 36.7 (CH_2); IR (neat): $\tilde{\nu}$ = 3426, 3060, 3026, 2384, 1495, 1454 cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{34}DBN_2$: C 83.21, H 8.11, N 6.26; found: C 83.35, H 8.20, N 6.31.

(1*R*,2*R*,3*S*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-3-dimethylphenylsilyl-1-propylaziridine(N^1-*B*)-borane (6ab): colorless oil; R_f=0.50 (hexane/EtOAc 10:1); $[\alpha]_D^{25}$ = −28.9 (c = 0.98, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58–7.22 (m, 15H), 3.79 (AB syst., J=14.1 Hz, 4H), 3.61–3.51 (m, 1H), 2.87–2.75 (m, 1H), 2.21–1.82 (m, 3H), 1.59 (brs, 3H), 1.40–1.29 (m, 2H), 1.00 (d, J=5.4 Hz, 3H), 0.79 (t, J=5.9 Hz, 3H), 0.60 (s, 3H), 0.50 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.0 (2×C), 137.2 (C), 133.9 (2×CH), 129.3 (4×CH), 128.2 (CH), 128.1 (4×CH), 127.9 (2×CH), 126.7 (2×CH), 70.8 (CH_2), 56.0 (CH), 54.4 (2×CH_2), 53.5 (CH), 41.8 (CH), 19.7 (CH_2), 13.2 (CH_3), 11.2 (CH_3), −1.2 (CH_3), −1.6 (CH_3); IR (neat): $\tilde{\nu}$ = 3027, 2958, 2390, 2287, 1494, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 455 (<1) [M^+−H, 351 (60), 224 (38), 132 (29), 112 (49), 91 (100), 53 (45); HRMS (70 eV): m/z: calcd for $C_{29}H_{40}BN_2Si$: 455.3048, found 455.3057 [M^+−H].

(1*R*,2*R*,3*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)ethyl]-3-methylaziridine(N^1-*B*)-borane (6bc): colorless oil; R_f=0.59 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −4.9 (c = 1.79, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.20 (m, 10H), 6.20–6.06 (m, 1H), 5.26–5.09 (m, 2H), 3.82 (AB syst., J=14.1 Hz, 4H), 3.58–3.49 (m, 1H), 3.41 (dd, J=13.3, 6.7 Hz, 1H), 2.78 (dd, J=13.1, 7.1 Hz, 1H), 2.18–2.02 (m, 2H), 1.61 (brs, 3H), 1.31 (d, J=6.2 Hz, 3H), 1.09 (d, J=6.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.3 (2×C), 131.4 (CH), 128.7 (4×CH), 128.0 (4×CH), 126.7 (2×CH), 120.8 (CH_2), 68.4 (CH_2), 54.5 (2×CH_2), 51.9 (CH), 51.0 (CH), 42.2 (CH), 13.2 (CH_3), 9.2 (CH_3); IR (neat): $\tilde{\nu}$ = 3026, 2930, 2367, 1494, 1455 cm^{-1}; MS (70 eV, EI): m/z (%): 333 (<1) [M^+−H], 266 (12), 229 (33), 224 (18), 196 (22), 91 (100); HRMS (70 eV): m/z: calcd for $C_{22}H_{30}BN_2$: 333.2497, found 333.1495 [M^+−H].

(1*R*,2*R*,3*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)ethyl]-3-ethylaziridine(N^1-*B*)-borane (6bd): colorless oil; R_f=0.53 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −10.3 (c = 1.150, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.19 (m, 10H), 6.20–6.06 (m, 1H), 5.26–5.07 (m, 2H), 3.81 (AB syst., J= 14.1 Hz, 4H), 3.60–3.49 (m, 2H), 2.58 (dd, J=13.3, 7.3 Hz, 1H), 2.04 (apparent t, J=8.5 Hz, 1H), 1.94–1.79 (m, 2H), 1.53–1.46 (m, 1H), 1.29 (brs, 3H), 1.10–1.05 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3 (2×C), 131.7 (CH), 128.9 (4×CH), 128.0 (4×CH), 126.7 (2×CH), 120.6 (CH_2), 68.6 (CH_2), 54.5 (2×CH_2), 52.4 (2×CH), 48.4 (CH), 17.4 (CH_2), 13.2 (CH_3), 12.1 (CH_3); IR (neat): $\tilde{\nu}$ = 3027, 2931, 2367, 1495, 1455 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{33}BN_2$: C 79.31, H 9.55, N 8.04; found: C 79.45, H 9.45, N 8.12.

(1*R*,2*R*,3*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)ethyl]-3-trimethylsilylaziridine(N^1-*B*)-borane (6be): colorless oil; R_f=0.43 (hexane/EtOAc 10:1); $[\alpha]_D^{25}$ = −35.2 (c = 1.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.20 (m, 10H), 6.21–6.07 (m, 1H), 5.20 (d, J=10.0 Hz, 1H), 5.06 (d, J=17.3 Hz, 1H), 3.89 (d, J=14.0 Hz, 2H), 3.74 (d, J=14.0 Hz, 2H), 3.59–3.50 (m, 2H), 2.52 (dd, J=12.9, 7.7 Hz, 1H), 2.22 (apparent t, J= 9.8 Hz, 1H), 1.28 (brs, 3H), 1.22 (d, J=9.6 Hz, 1H), 1.06 (d, J=6.9 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2 (2×C), 131.9 (CH), 129.0 (4×CH), 128.1 (4×CH), 126.7 (2×CH), 120.5 (CH_2), 70.2 (CH_2), 54.8 (CH), 54.5 (2×CH_2), 53.7 (CH), 40.5 (CH), 13.0 (CH_3), −0.2 (3×CH_3); IR (neat): $\tilde{\nu}$ = 3026, 2957, 2392, 2286, 1493, 1451, 1250 cm^{-1}; MS (70 eV, EI): m/z (%): 391 (2) [M^+−H], 287 (64), 224 (45), 132 (49), 91 (100), 53 (45); HRMS (70 eV): m/z: calcd for $C_{24}H_{36}BN_2Si$: 391.2735, found 391.2741 [M^+−H]; elemental analysis calcd (%) for $C_{24}H_{37}BN_2Si$: C 73.45, H 9.50, N 7.14; found: C 73.59, H 9.41, N 7.28.

(1*R*,2*R*,3*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)ethyl]-3-methylaziridine-(N^1-*B*)-borane (6cc): colorless oil; R_f=0.50 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −22.6 (c = 0.91, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.24 (m, 15H), 4.15 (d, J=13.2 Hz, 1H), 3.84 (AB syst., J=14.6 Hz, 4H), 3.76–3.61 (m, 2H), 2.25 (apparent q, J=8.5 Hz, 1H), 2.17 (apparent t, J= 8.7 Hz, 1H), 1.48 (brs, 3H), 1.36 (d, J=6.2 Hz, 3H), 1.11 (d, J=6.8 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.3 (2×C), 132.2 (C), 131.4, 129.5, 128.6, 128.2, 128.0, 126.6 (15×CH), 67.0 (CH_2), 54.3 (2×CH_2), 51.7 (CH), 48.2 (CH), 40.8 (CH), 13.7 (CH_3), 9.0 (CH_3); IR (neat): $\tilde{\nu}$ = 3012, 2930, 2364, 1495, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 384 (<1) [M^+],

279 (90), 224 (31), 196 (32), 160 (21), 91 (100); HRMS (70 eV): *m/z*: calcd for $C_{26}H_{33}BN_2$: 384.2737, found 384.2731 [M^+].

(1*R*,2*R*,3*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)ethyl]-3-ethylaziridine(*N*^{1}-*B*)-borane (6cd): colorless oil; R_f=0.48 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −14.0 (*c* = 1.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.18 (m, 15H), 4.16 (d, *J*=13.1 Hz, 1H), 3.80 (AB syst., *J*=14.1 Hz, 4H), 3.68–3.56 (m, 2H), 2.12 (apparent t, *J*=8.7 Hz, 1H), 2.03–1.84 (m, 2H), 1.58–1.47 (m, 1H), 1.31 (brs, 3H), 1.05 (d, *J*=6.9 Hz, 3H), 0.99 (t, *J*= 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.3 (2×C), 132.2 (C), 131.8, 128.9, 128.5, 128.2, 128.0, 126.7 (15×CH), 67.3 (CH_2), 54.4 (2× CH_2), 52.2 (CH), 49.4 (CH), 46.8 (CH), 17.4 (CH_2), 13.7 (CH_3), 12.2 (CH_3); MS (70 eV, EI): *m/z* (%): 293 (60) [M^+−C_7H_7−BH_3], 224 (23), 196 (25), 160 (30), 91 (100); IR (neat): $\tilde{\nu}$ = 3028, 2931, 2370, 1495, 1454 cm^{-1}; HRMS (70 eV): *m/z*: calcd for $C_{20}H_{25}N_2$: 293.2018, found 293.2017 [M^+−C_7H_7−BH_3]; elemental analysis calcd (%) for $C_{27}H_{35}BN_2$: C 81.40, H 8.86, N 7.03; found: C 81.61, H 8.73, N 7.09.

(1*R*,2*S*,3*S*,1′*S*)-1-Allyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]-3-trimethylsylilaziridine(*N*^{1}-*B*)-borane (6de): Data on the 65:35 mixture of diastereoisomers: colorless oil; R_f=0.52 (hexane/EtOAc 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.23 (m, 10H), 6.54–6.41 (m, 1H, minor isomer), 6.36–6.22 (m, 1H, major isomer), 5.43–5.19 (m, 2H), 3.95 (s, 4H), 3.85 (d, *J*=3.7 Hz, 4H, minor isomer), 3.69 (dd, *J*=6.6, 6.2 Hz, 1H), 3.46–3.34 (m, 1H), 2.84 (dd, *J*=13.1, 7.7 Hz, 1H), 2.38 (apparent t, *J*=8.3 Hz, 1H), 1.71–1.54 (m, 3H), 1.54 (brs, 3H), 1.47 (d, *J*=8.5 Hz, 1H, minor isomer), 1.31(d, *J*=10.2 Hz, 1H, major isomer), 0.95 (d, *J*= 6.7 Hz, 3H, major isomer), 0.87 (d, *J*=6.7 Hz, 3H, minor isomer), 0.60 (d, *J*=6.6 Hz, 3H, major isomer), 0.55 (d d, *J*=6.74 Hz, 3H, minor isomer), 0.25 (s, 9H, major isomer), 0.23 (s, 9H, minor isomer); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 (2×C, major isomer), 140.2 (2×C, minor isomer), 133.1 (CH, minor isomer), 131.8 (CH, major isomer), 129.3 (4× CH), 127.9 (4×CH), 126.6 (2×CH), 120.9 (CH_2, major isomer), 120.0 (CH_2, minor isomer), 70.9 (CH_2, major isomer), 64.9 (CH_2, minor isomer), 55.3 (CH, major isomer), 54.5 (CH, major isomer), 54.3 (2× CH_2, major isomer), 53.9 (2×CH_2, minor isomer), 51.6 (CH, minor isomer), 44.7 (CH, minor isomer), 41.4 (CH), 41.2 (CH_2, minor isomer), 41.0 (CH_2, major isomer), 24.4 (CH, minor isomer), 24.3 (CH_3, major isomer), 24.2 (CH, major isomer), 23.5 (CH_3, minor isomer), 21.3 (CH_3, minor isomer), 21.2 (CH_3, major isomer), 0.2 (3×CH_3, major isomer), −1.1 (3×CH_3, minor isomer); IR (neat): $\tilde{\nu}$ = 3029, 2954, 2867, 2374, 1495, 1456, 1251 cm^{-1}; MS (70 eV, EI): *m/z* (%): 433 (4) [M^+−H], 329 (74), 266 (92), 184 (79), 152 (67), 91 (100), 73 (62); HRMS (70 eV): *m/z*: calcd for $C_{27}H_{42}BN_2Si$: 433.3248, found 433.3216 [M^+−H].

(1*R*,2*S*,3*S*,1′*S*)-1-Cyclohexyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]-3-methylaziridine(*N*^{1}-*B*)-borane (6ec): colorless oil; R_f=0.49 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −35.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.10 (m, 10H), 3.90 (AB syst., *J*=13.9 Hz, 4H), 3.45 (apparent t, *J*=9.5 Hz, 1H), 2.24–2.17 (m, 3H), 2.12–2.04 (m, 4H), 1.89–1.56 (m, 9H), 1.31 (d, *J*=6.3 Hz, 3H), 1.22–1.09 (m, 3H), 0.92 (d, *J*= 6.7 Hz, 3H), 0.49 (d, *J*=6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5 (2×C), 129.3 (4×CH), 127.8 (4×CH), 126.6 (2×CH), 77.5 (CH), 53.5 (2×CH_2), 52.2 (CH), 50.2 (CH), 44.6 (CH), 40.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 25.7 (2×CH_2), 25.5 (CH_2), 24.0 (CH and CH_3), 20.7 (CH_3), 9.9 (CH_3); MS (70 eV, EI): *m/z* (%): 417(1) [M^+−H], 313 (25), 266 (24), 194 (21), 91 (100), 55 (19); IR (neat): $\tilde{\nu}$ = 3442, 2931, 2355, 1651, 1494, 1454 cm^{-1}; HRMS (70 eV): *m/z*: calcd for $C_{28}H_{42}BN_2$: 417.3436, found 417.3430 [M^+−H]; elemental analysis calcd (%) for $C_{28}H_{43}BN_2$: C 80.36, H 10.36, N 6.69; found: C 80.51, H 10.43, N 6.61.

(1*R*,2*S*,3*S*,1′*S*)-1-Cyclohexyl-2-[1′-(dibenzylamino)-3′-(methyl)butyl]-3-trimethylsylilaziridine(*N*^{1}-*B*)-borane (6ee): Colorless oil; R_f=0.33 (hexane/EtOAc 10:1); $[\alpha]_D^{25}$ = −30.3 (*c* = 0.98, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.19 (m, 10H), 3.94 (AB syst., *J*=13.3 Hz, 4H), 3.54.3.46 (m, 1H), 2.39 (apparent t, *J*=9.8 Hz, 1H), 2.15–2.02 (m, 3H), 1.88–1.52 (m, 4H), 1.48.1.34 (m, 9H), 0.93 (d, *J*=6.6 Hz, 3H), 0.91–0.84 (m, 2H), 0.51 (d, *J*=6.6 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7 (2×C), 129.5 (4×CH), 127.8 (4×CH), 126.6 (2×CH), 72.0 (CH), 55.0 (CH), 54.0 (CH), 53.2 (2×CH_2), 44.0 (CH), 39.9 (CH_2), 31.2 (CH_2), 29.4 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 25.4 (CH_2), 24.3 (CH), 24.0 (CH_3), 21.0 (CH_3), 0.7 (3×CH_3); IR (neat): $\tilde{\nu}$ = 3036, 2958, 2390, 1603, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 475 (<1) [M^+−H], 371 (9), 266 (33), 210 (12), 91 (100), 57 (31); HRMS (70 eV): *m/z*: calcd for $C_{30}H_{48}BN_2Si$: 475.3674, found 475.3677 [M^+−H]; elemental analysis calcd (%) for $C_{30}H_{49}BN_2Si$: C 75.60, H 10.36, N 5.88; found: C 75.81, H 10.44, N 5.78.

(1*R*,2*S*,3*S*,1′*S*)-2-[1′-(Dibenzylamino)-3′-(phenyl)ethyl]-3-methyl-1-propylaziridine(*N*^{1}-*B*)-borane (6gc): Colorless oil; R_f=0.51 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −21.9 (*c* = 1.13, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.09 (m, 15H), 3.95 (AB syst., *J*=14.1 Hz, 4H), 3.63–3.49 (m, 1H), 2.99 (dd, *J*=13.5, 5.4 Hz, 1H), 2.65 (dd, *J*=13.5, 9.3 Hz, 1H), 2.10–1.83 (m, 3H), 1.79–1.68 (m, 3H), 1.32 (brs, 3H), 0.83 (t, *J*= 7.1 Hz, 3H), 0.69 (d, *J*=6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (2×C), 138.5 (C), 129.5 (2×CH), 129.1 (4×CH), 128.2 (2×CH), 127.9 (4×CH), 126.7 (2×CH), 126.2 (CH), 69.0 (CH_2), 58.2 (CH), 54.7 (2×CH_2), 51.4 (CH), 44.4 (CH), 36.3 (CH_2), 19.4 (CH_2), 11.2 (CH_3), 9.0 (CH_3); IR (neat): $\tilde{\nu}$ = 3026, 2932, 2369, 1602, 1495, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 411 (<1) [M^+−H], 307 (43), 201 (23), 91 (100), 65 (21); HRMS (70 eV): *m/z*: calcd for $C_{28}H_{36}BN_2$: 411.2966, found 411.2975 [M^+−H].

(1*R*,2*S*,3*S*,1′*S*)-1-Cyclohexyl-2-[1′-(dibenzylamino)-3′-(phenyl)ethyl]-3-dimethylphenylsylilaziridine(*N*^{1}-*B*)-borane (6hb): Colorless oil; R_f=0.48 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −21.4 (*c* = 0.94, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.03 (m, 20H), 4.00–3.95 (m, 1H), 3.85 (AB syst., *J*=13.8 Hz, 4H), 2.96–2.73 (m, 3H), 2.45 (apparent t, *J*= 9.6 Hz, 1H), 2.11–2.05 (m, 2H), 1.87–1.63 (m, 5H), 1.52 (d, *J*=9.8 Hz, 1H), 1.27 (brs, 3H), 1.23–1.09 (m, 2H), 0.90–0.87 (m, 1H), 0.66 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.0 (3×C), 138.1 (C), 134.0 (2×CH), 132.9 (CH), 129.6 (2×CH), 129.2 (4×CH), 128.1 (2× CH), 127.9 (2×CH), 127.7 (4×CH), 126.5 (2×CH), 126.2 (CH), 78.8 (CH), 56.9 (CH), 54.9 (CH), 53.9 (2×CH_2), 43.6 (CH), 38.0 (CH_2), 30.2 (CH_2), 29.2 (CH_2), 25.8 (2×CH_2), 25.4 (CH_2), −0.5 (CH_3), −0.7 (CH_3); IR (neat): $\tilde{\nu}$ = 3084, 3064, 3028, 2377, 2285, 1494, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 459 (24) [M^+−C_7H_7−BH_3], 333 (9), 300 (10), 228 (11), 135 (14), 91 (100); HRMS (70 eV): *m/z*: calcd for $C_{31}H_{39}N_2Si$: 467.2877, found 467.2877 [M^+−C_7H_7−BH_3]; elemental analysis calcd (%) for $C_{38}H_{49}BN_2Si$: C 79.69, H 8.62, N 4.89; found: C 79.91, H 8.51, N 4.96.

(1*R*,2*S*,3*S*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-3′-(phenyl)ethyl]-3-methylaziridine(*N*^{1}-*B*)-borane (6ic): Colorless oil; R_f=0.54 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −22.9 (*c* = 0.82, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45–7.01 (m, 20H), 4.13 (d, *J*=13.3 Hz, 1H), 3.88 (s, 4H), 3.70 (d, *J*=13.3 Hz, 1H), 2.96 (dd, *J*=13.9, 6.1 Hz, 1H), 2.61 (dd, *J*= 13.3, 8.0 Hz, 1H), 2.27–2.08 (m, 2H), 1.32 (brs, 3H), 0.94–0.90 (m, 1H), 0.72 (d, *J*=5.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.9 (2×C), 138.5 (C), 132.2 (C), 131.5, 129.5, 129.1, 128.8, 128.3, 128.2, 128.0, 126.7, 126.2 (20×CH), 67.4 (CH_2), 58.1 (CH), 54.2 (2×CH_2), 47.6 (CH), 42.0 (CH), 36.4 (CH_2), 8.8 (CH_3); IR (neat): $\tilde{\nu}$ = 3084, 3062, 3027, 2377, 2285, 1495, 1454 cm^{-1}; MS (70 eV, EI): *m/z* (%): 459 (<1) [M^+−H], 356 (39), 355 (87), 264 (40), 250 (31), 173 (40), 91 (100); HRMS (70 eV): *m/z*: calcd for $C_{32}H_{36}BN_2$: 459.2966, found 459.2962 [M^+−H].

(2*R*,3*R*,1′*S*)-1-Allyl-2-[(1′-dibenzylamino)ethyl]-3-methylaziridine (7bc): Colorless oil; R_f=0.55 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −12.1 (*c* = 0.90, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.21 (m, 10H), 6.17–6.04 (m, 1H), 5.33–5.17 (m, 2H), 3.85 (AB syst., *J*=14.0 Hz, 4H), 3.27 (dd, *J*=13.6, 5.6 Hz, 1H), 2.76 (dd, *J*=14.0, 5.5 Hz, 1H), 2.67 (dd, *J*=9.4, 6.9 Hz, 1H), 1.55 (dd, *J*=9.3, 7.0 Hz, 1H), 1.38–1.31 (m, 1H), 1.10 (d, *J*= 6.9 Hz, 3H), 1.06 (d, *J*=5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 (2×C), 136.1 (CH), 128.6 (4×CH), 127.9 (4×CH), 126.4 (2×CH), 116.1 (CH_2), 63.5 (CH_2), 54.0 (2×CH_2), 52.9 (CH), 45.5 (CH), 36.5 (CH), 15.8 (CH_3), 13.6 (CH_3); IR (neat): $\tilde{\nu}$ = 3028, 2964, 2927, 1494, 1455 cm^{-1}; MS (70 eV, EI): *m/z* (%): 320 (<1) [M^+], 229 (89), 224 (37), 196 (51), 91 (100); HRMS (70 eV): *m/z*: calcd for $C_{22}H_{18}N_2$: 320.2247, found 320.2248 [M^+]; elemental analysis calcd (%) for $C_{22}H_{28}N_2$: C 82.45, H 8.81, N 8.74; found: C 82.65, H 8.99, N 8.65.

(2*R*,3*R*,1′*S*)-1-Allyl-2-[(1′-dibenzylamino)ethyl]-3-ethylaziridine (7bd): Colorless oil; R_f=0.60 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −16.3 (*c* = 1.11, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.22 (m, 10H), 6.16–6.02 (m, 1H), 5.28–5.15 (m, 2H), 3.85 (AB syst., *J*=14.1 Hz, 4H), 3.38 (dd, *J*=13.2, 6.2 Hz, 1H), 2.73–2.59 (m, 2H), 1.58 (dd, *J*=9.4, 6.4 Hz, 1H),

1.35–1.20 (m, 3H), 1.10 (d, $J=6.8$ Hz, 3H), 0.99 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 (2×C), 136.4 (CH), 128.7 (4×CH), 127.9 (4×CH), 126.4 (2×CH), 116.3 (CH_2), 64.0 (CH_2), 54.1 (2×CH_2), 53.0 (CH), 46.3 (CH), 43.8 (CH), 21.5 (CH_2), 15.1 (CH_3), 12.4 (CH_3); IR (neat): $\tilde{\nu}$ = 3027, 2965, 2927, 1494, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 334 (<1) [M^+], 243 (69), 224 (32), 196 (42), 110 (36), 91 (100); HRMS (70 eV): m/z: calcd for $C_{23}H_{30}N_2$: 334.2404, found 334.2403 [M^+].

(2*R*,3*S*,1′*S*)-1-Allyl-2-[(1′-dibenzylamino)ethyl]-3-trimethylsilylaziridine (7be): Colorless oil; R_f=0.38 (hexane/EtOAc 10:1); $[\alpha]_D^{25}$ = −12.3 (c = 3.11, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.21 (m, 10H), 6.13–6.00 (m, 1H), 5.25–5.12 (m, 2H), 3.84 (AB syst., $J=13.9$ Hz, 4H), 3.56 (dd, $J=13.3$, 5.8 Hz, 1H), 2.54–2.39 (m, 2H), 1.76 (dd, $J=9.6$, 7.5 Hz, 1H), 1.12 (d, $J=6.9$ Hz, 3H), 0.32 (d, $J=7.3$ Hz, 1H), −0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7 (2×C), 136.7 (CH), 128.6 (4×CH), 127.9 (4×CH), 126.4 (2×CH), 116.1 (CH_2), 66.7 (CH_2), 54.6 (CH), 53.8 (2×CH_2), 47.8 (CH), 32.9 (CH), 15.7 (CH_3), −1.4 (3×CH_3); IR (neat): $\tilde{\nu}$ = 3027, 2955, 1494, 1454, 1364, 1248 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{34}N_2Si$: C 76.13, H 9.50, N 7.14; found: C 76.31, H 9.39, N 7.21.

(2*R*,3*R*,1′*S*)-1-Allyl-2-[(1′-dibenzylamino)-3′-(methyl)butyl]-3-deuterioaziridine (7da): Colorless oil; R_f=0.41 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −70.3 (c = 0.92, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.20 (m, 10H), 6.17–6.00 (m, 1H), 5.33–5.18 (m, 2H), 3.82 (AB syst., $J=13.8$ Hz, 4H), 3.12 (dd, $J=13.6$, 5.6 Hz, 1H), 2.86 (dd, $J=13.6$, 5.6 Hz, 1H), 2.52–2.41 (m, 1H), 1.86–1.74 (m, 1H), 1.62 (apparent t, $J=7.1$ Hz, 1H), 1.58–1.44 (m, 1H), 1.29 (d, $J=4.1$ Hz, 1H), 1.08–0.94 (m, 1H), 0.83 (d, $J=6.6$ Hz, 3H), 0.49 (d, $J=6.6$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.5 (2×C), 135.9 (CH), 128.9 (4×CH), 127.8 (4×CH), 126.5 (2×CH), 116.2 (CH_2), 63.4 (CH_2), 57.0 (CH), 53.9 (2×CH_2), 39.5 (CH), 38.9 (CH_2), 30.4 (CHD, t, $J=25.2$ Hz), 24.1 (CH), 23.4 (CH_3), 21.3 (CH_3); IR (neat): $\tilde{\nu}$ = 3063 3028, 2953, 2866, 1656, 1495, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 349 (1) [M^+], 266 (37), 258 (38), 196 (75), 91 (100); HRMS (70 eV): m/z: calcd for $C_{24}H_{31}DN_2$: 349.2622, found 349.2624 [M^+]; elemental analysis calcd (%) for $C_{24}H_{31}DN_2$: C 62.47, H 9.52, N 8.01; found: C 62.61, H 9.44, N 8.10.

(2*R*,3*R*,1′*S*)-1-Benzyl-2-[1′-(dibenzylamino)-3′-(phenyl)ethyl]-3-methylaziridine (7ic): Colorless oil; R_f=0.47 (hexane/EtOAc 10:1); $[\alpha]_D^{25}$ = −26.7 (c = 0.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–6.97 (m, 20H), 3.93 (d, $J=13.3$ Hz, 1H), 3.74 (AB syst., $J=13.5$ Hz, 4H), 3.37 (d, $J=13.3$ Hz, 1H), 2.91 (dd, $J=12.7$, 3.1 Hz, 1H), 2.83–2.76 (m, 1H), 2.69 (dd, $J=12.7$, 6.9 Hz, 1H), 1.76 (dd, $J=9.1$, 6.8 Hz, 1H), 1.42–1.32 (m, 1H), 0.75 (d, $J=5.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.1 (2×C), 140.3 (2×C), 130.0, 129.3, 129.0, 128.8, 128.3, 128.2, 127.4, 126.9, 126.2 (20×CH), 65.4 (CH_2), 57.5 (CH), 54.2 (2×CH_2), 44.3 (CH), 38.7 (CH_2), 38.1 (CH), 13.9 (CH_3); IR (neat): $\tilde{\nu}$ = 3062, 3027, 2958, 2925, 1603, 1494, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 446 (<1) [M^+], 356 (56), 355 (95), 300 (62), 264 (48), 173 (45), 91 (100); HRMS (70 eV): m/z: calcd for $C_{32}H_{34}N_2$: 446.2716, found 446.2708 [M^+].

(1*R*,2*S*,3*R*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-3-deuterio-3-methyl-1-propylaziridine(N^1-*B*)-borane (12aac): Colorless oil; R_f=0.56 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −59.0 (c = 0.61, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.51–7.21 (m, 10H), 3.78 (AB syst., $J=14.1$ Hz, 4H), 3.64–3.53 (m, 1H), 2.63 (ddd, $J=16.7$, 11.5, 4.9 Hz, 1H), 2.34 (ddd, $J=17.2$, 11.5, 5.6 Hz, 1H), 2.08–1.76 (m, 3H), 1.33 (br s, 3H), 1.31 (s, 3H), 1.12 (d, $J=6.9$ Hz, 3H), 0.93 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.8 (2×C), 128.7 (4×CH), 128.0 (4×CH), 126.8 (2×CH), 58.6 (CH_2), 56.8 (CH), 54.4 (2×CH_2), 52.4 (CH), 51.9 (CHD, d, $J=26.5$ Hz), 20.0 (CH_2), 13.4 (CH_3), 11.6 (CH_3), 11.5 (CH_3); IR (neat): $\tilde{\nu}$ = 3029, 2933, 2366, 1495, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 336 (1) [M^+−H], 232 (36), 231 (42), 224 (51), 196 (36), 91 (100); HRMS (70 eV): m/z: calcd for $C_{22}H_{31}DBN_2$: 336.2716, found 336.2719 [M^+−H]; elemental analysis calcd (%) for $C_{22}H_{32}DBN_2$: C 78.33, H 10.16, N 8.30; found: C 78.53, H 9.98, N 8.38.

(1*R*,2*S*,3*R*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-3-deuterio-3-ethyl-1-propylaziridine(N^1-*B*)-borane (12aad): Colorless oil; R_f=0.59 (hexane/EtOAc 3:1); $[\alpha]_D^{25}$ = −18.4 (c = 1.13, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.24 (m, 10H), 3.79 (AB syst., $J=13.8$ Hz, 4H), 3.66–3.59 (m, 1H), 2.73 (ddd, $J=16.6$, 11.8, 4.8 Hz, 1H), 2.35 (ddd, $J=16.9$, 11.7, 5.1 Hz, 1H), 2.12–2.00 (m, 1H), 1.95 (d, $J=7.0$ Hz, 1H), 1.91–1.78 (m, 2H), 1.61 (br s, 3H), 1.44–1.31 (m, 1H), 1.13 (d, $J=6.9$ Hz, 3H), 1.07 (t, $J=7.5$ Hz, 3H), 0.94 (t, $J=7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.8 (2×C), 128.8 (4×CH), 128.1 (4×CH), 126.8 (2×CH), 58.9 (CH_2), 56.2 (CH), 54.4 (2×CH_2), 52.7 (CHD, d, $J=26.9$ Hz), 52.2 (CH), 20.2 (CH_2), 20.0 (CH_2), 13.6 (CH_3), 11.5 (2×CH_3); IR (neat): $\tilde{\nu}$ = 3028, 2931, 2367, 1494, 1454 cm^{-1}; MS (70 eV, EI): m/z (%): 350 (3) [M^+−H], 246 (38), 224 (43), 132 (31), 113 (38), 91 (100); HRMS (70 eV): m/z: calcd for $C_{23}H_{33}DBN_2$: 350.2872, found 350.2874 [M^+−H].

(1*R*,2*S*,3*R*,1′*S*)-2-[1′-(Dibenzylamino)ethyl]-3-deuterio-3-trimethylsilyl-1-propylaziridine(N^1-*B*)-borane (12aae): Colorless oil; R_f=0.50 (hexane/EtOAc 10:1); $[\alpha]_D^{25}$ = −13.9 (c = 0.38, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.46–7.24 (m, 10H), 3.80 (AB syst., $J=13.9$ Hz, 4H), 3.67–3.52 (m, 1H), 3.01–2.89 (m, 1H), 2.19–1.87 (m, 3H), 1.85–1.70 (m, 1H), 1.30 (br s, 3H), 1.09 (d, $J=7.1$ Hz, 3H), 0.90 (t, $J=6.9$ Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.9 (2×C), 129.0 (4×CH), 128.1 (4×CH), 126.8 (2×CH), 64.1 (CH_2), 54.6 (2×CH_2), 54.2 (CH), 53.7 (CH), 20.7 (CH_2), 13.9 (CH_3), 11.4 (CH_3), −1.2 (3×CH_3 and CHD, d, $J=26.7$ Hz); IR (neat): $\tilde{\nu}$ = 3027, 2963, 2378, 2275, 1494, 1454, 1254 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{38}DBN_2Si$: C 72.89, H 10.19, N 7.08; found: C 72.99, H 10.25, N 6.97.

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