Highly Diastereo- and Enantioselective Aziridination of α,β-Unsaturated Amides with Diaziridine and Mechanistic Consideration on Its Stereochemistry

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Dedicated to Prof. *Dieter Seebach* on the occasion of his 65th birthday

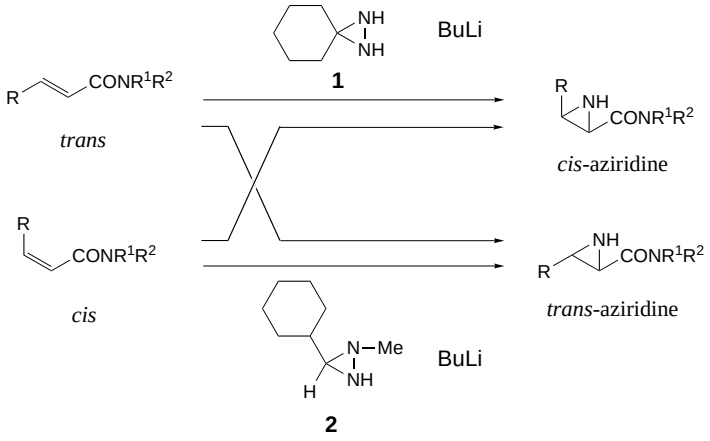
During studies of aziridination of α,β-unsaturated amides with diaziridine, we found that we could prepare both the *cis*- and *trans*-aziridinecarboxamides by choosing an appropriately substituted diaziridine. While 3-monosubstituted diaziridine **2** was suitable for the *trans*-selective aziridination, employment of 3,3-dialkyldiaziridine **1** resulted in the formation of *cis*-aziridine carboxamides, irrespective of the geometry of the substrate (*Scheme 1* and *Tables 1* and *2*). To elucidate the unique nonstereospecificity and to expand these aziridinations to asymmetric ones, several optically active diaziridines were newly prepared. Aziridination with an optically active 3-monosubstituted diaziridine, 3-cyclohexyl-1-[(1*R*)-1-phenylethyl]diaziridine **16**, proceeded smoothly with high *trans*-selectivity as well as excellent enantioselectivity (up to 98% ee; see *Table 3*). On the other hand, highly enantioselective *cis*-aziridination was achieved (> 99% ee) with optically active 3,3-dimethyl-1-[(1*R*)-1-phenylethyl]diaziridine **15**, though the yield was low (4%). This aziridination was considered to proceed stepwise by way of the enolate intermediate (*Scheme 2*). Careful inspection of the stereochemistry and its solvent-dependence suggested that the diastereoselection of the reaction was kinetically controlled: the 1,4-addition of *N*-lithiated diaziridine was a crucial step for determination of the stereochemical course of the aziridination (*Figs. 2–4*).

Introduction. – Aziridines are versatile synthetic intermediates for N-containing compounds [1]. One of the most straightforward methods for their synthesis is addition of a nitrene or nitrenoid to olefins. Enantioselective nitrene-transfer aziridination in the presence of chiral copper, manganese, and ruthenium catalysts has recently been reported [2]. In these reactions, [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs) or a derivative is employed as the nitrene precursor, and the resulting aziridines are *N*-(*p*-toluenesulfonyl)ated. However, it is difficult to remove the *p*-toluenesulfonyl group without causing decomposition of the aziridine ring. Another conventional method for aziridination is the 1,4-addition of an *O*-substituted hydroxylamine derivative to α,β-unsaturated carbonyl compounds and the subsequent enolate cyclization [3]. By these methods, optically active *N*-unsubstituted aziridines are accessible, but the major products are thermodynamically stable *trans*-aziridines, even in the reaction of *cis*-α,β-unsaturated carbonyl compounds. Still, *cis*-selective aziridination remains unsettled.

To explore the potential of the latter method, we examined the use of diaziridine as an amine nucleophile in place of *O*-substituted hydroxylamine. Although there was no previous example of the use of diaziridine as an N-donor, diaziridine was expected to be

highly nucleophilic due to the presence of two vicinal N-atoms (α-effect). Furthermore, it was expected that its N–N bond would be cleaved readily due to the strain energy of the three-membered ring. Thus, we examined the reaction of diaziridine and α,β-unsaturated amide under various reaction conditions and disclose now a unique reagent-controlled stereoselective aziridination as shown in *Scheme 1*. We describe in detail here the stereoselective aziridination with racemic or optically active diaziridines and discuss the mechanism of the stereoselection[1]).

Scheme 1. *Reagent-Controlled Diastereoselectivity in Aziridination with Diaziridines*



***cis*-Selective Aziridination of α,β-Unsaturated Amides** (*Table 1*). – Examination of the aziridination of α,β-unsaturated amides commenced with 3,3-pentamethylenediaziridine (=1,2-diazaspiro[2.5]octane; **1**), which was readily available from cyclohexanone by treatment with hydroxylamine-*O*-sulfonic acid in aqueous ammonia [5a]. Diaziridine **1** itself did not undergo the desired 1,4-addition at room temperature. However, *N*-lithiated **1**, prepared by treatment of **1** with 1 equiv. of butyllithium (BuLi) at $-78°$, readily reacted with α,β-unsaturated amides **3**–**10**, **12**, and **14** to give 2,3-*cis*-aziridinecarboxamides (*Table 1*). Although many hydroxylamine or hydrazine derivatives have been reported to add to α,β-unsaturated carbonyl compounds, the resulting 1,4-adducts do not undergo the subsequent ring closure to give the desired aziridine under the addition-reaction conditions. *Lewis* acid or base treatment is required for further conversion of the 1,4-adducts to aziridines. On the other hand, the present reaction directly gives the desired aziridine under the addition-reaction conditions. The configuration of the aziridine obtained from **9** was confirmed to be 2,3-*cis* by chemical correlation to the corresponding 2,3-*cis*-*N*-(*p*-toluenesulfonyl)aziridinecarboxamide, which was prepared independently by a reported method [6]. The coupling constant between methine protons at the aziridine ring was 7.5 Hz for the *cis*-aziridinecarboxamide, while 4.0 Hz was observed for the *trans*-aziridinecarboxamide. These observations are consistent with the coupling constants predicted by the *Karplus* equation. Thus, the geometry of other aziridinecarboxamides described in *Table 1* was assigned

[1]) Preliminary results have been communicated in [4].

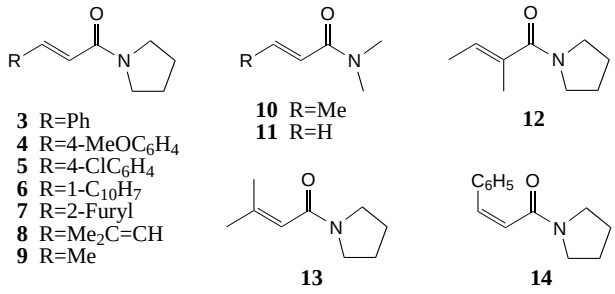


Table 1. cis-*Selective Aziridination of α,β-Unsaturated Amides with* **1**[a])

Entry	Substrate	Time [h]	Yield [%][b])
1	**3**	11	97 (72)[c])
2	**4**	3	99
3	**5**	4	98
4	**6**	4	86
5	**7**	16	78
6	**8**	4	83
7	**9**	24	99 (82)[c])
8	**10**	24	89 (63)[c])
9	**11**	18	40 (39)[c])
10	**12**	24	30
11[d])	**13**	6	70
12	**14**	8	52 (39)[c])

[a]) All the reactions were conducted in THF at −30° with 2 equiv. of diaziridine **1** and BuLi unless otherwise noted. [b]) Isolated yields of the corresponding *cis*-aziridinecarboxamides after silica-gel column chromatography. Isomeric *trans*-aziridinecarboxamide could not be isolated. [c]) The previously reported result is cited in parentheses. [d]) The reaction was conducted at 0°. No aziridination occurred at −30°.

by their ^{1}H-NMR analyses[2]). All the reactions showed remarkably high *cis*-selectivity, and no *trans*-isomer was isolated in these reactions.

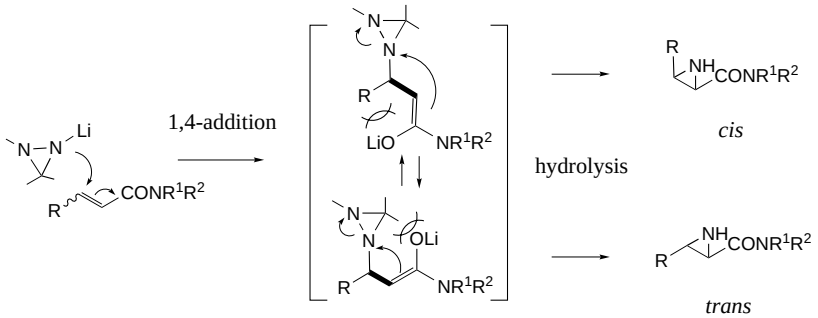
Although we previously communicated that the aziridination was carried out at −78° to room temperature, we found that better yields could be obtained by carrying out the reaction with 2 equiv. of *N*-lithiated **1** in THF at −30°. The yields of the aziridination of cinnamamide derivatives were more than 97% (*Entries 1–3*). The yield of the aziridine from acrylamide **11** was moderate and formation of unidentified by-products was detected (*Entry 9*). The reactions of trisubstituted olefin **12** and *cis*-cinnamamide derivative **14** were relatively slow, and yields of the corresponding *cis*-aziridines were somewhat reduced (*Entries 10* and *12*). Again, formation of *trans*-isomers was not detected. Accordingly, *cis*-selectivity in this reaction was independent on the geometry of the substrate used. Unfortunately, the reactions of other *α,β*-

[2]) The relative configurations of the aziridines obtained from trisubstituted *α,β*-unsaturated amide **12** were confirmed by NOESY measurements. The *trans*-isomer showed an NOE between the Me–C(2) and Me–C(3) groups.

unsaturated carbonyl compounds such as α,β-unsaturated aldehydes, ketones, or esters did not give the desired products in acceptable yields under the present conditions.

It is reasonable to consider that a two-step reaction mechanism is applicable to the present aziridination as shown in *Scheme 2*. Namely, *N*-lithiated **1** attacks the C(β) atom of α,β-unsaturated amides diastereoselectively to produce an enolate intermediate. Note that the N-atom introduced at C(β) is chiral. Subsequent intramolecular substitution gives *cis*-aziridine from the conformer that does not suffer severe steric interaction between one of the two geminal substituents of the diaziridine and the amide enolate moiety upon cyclization. This consideration further led us to the idea that *trans*-selectivity would be realized if one of the geminal substituents was removed: the enolate conformation was considered to be dictated by the steric repulsion between R and the amide enolate moiety. Accordingly, aziridination with a 3-monosubstituted diaziridine was next examined.

Scheme 2. *Stepwise Mechanism for the Aziridination with* N-*Lithiated Diaziridine.* For convenience, substituents or H-atoms at the diaziridine are represented by straight lines.



***trans*-Selective Aziridination of α,β-Unsaturated Amides** (*Table 2*). – As a 3-monosubstituted diaziridine, 1-methyl-3-cyclohexyldiaziridine (**2**) was prepared from cyclohexanecarboxaldehyde, methylamine, and hydroxylamine-*O*-sulfonic acid [5] or chloramine [7]. Aziridination was carried out under the conditions described in the preceding section. As expected, *trans*-aziridine was preferentially obtained in 52%, *e.g.* from *N*-(*E*)-cinnamoylpyrrolidine (**3**), together with a small amount of *cis*-aziridine (21%) as shown in *Table 2*, *Entry 1*. Furthermore, it was found that the aziridination at $-78°$ increased *trans*-selectivity up to 5.6:1 (*Entry 2*). Employment of a less-polar solvent further increased the selectivity, and the *trans*-isomer was obtained exclusively in toluene (*Entry 4*). It is, however, noteworthy that the ratio of *trans*- and *cis*-aziridines varied from 3:1 to 1:3 by switching the solvent from THF to toluene in the aziridination of *N*-(*Z*)-cinnamoylpyrrolidine (**14**) (*Entries 15* and *17*). The geometry of the (*Z*)-substrate was considered to be reflected in the configuration of the product of this reaction in less polar toluene. Chelate formation of the enolate intermediate in such a nonpolar solvent was attributable to this stereochemical outcome. The other substrates (**3**–**10** and **12**) were also converted preferentially to the corresponding *trans*-aziridines though the yields of the aziridines from **8**–**10** and **12** bearing a β-alkyl or β-alkenyl substituent were moderate (*Entries 8–14*).

Table 2. trans-*Selective Aziridination of α,β-Unsaturated Amides with* **2**[a])

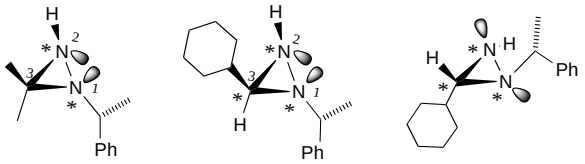
Entry	Substrate	Solvent	Temperature [°]	Time [h]	Yield [%][b]) *trans*	*cis*
1	**3**	THF	– 30	24	52	21
2	**3**	THF	– 78	4	78	14
3	**3**	ether	– 78	4	86	5
4	**3**	toluene	– 78	4	74	< 1
5	**4**	toluene	– 78	4	58	< 1
6	**5**	toluene	– 78	4	76	3
7	**6**	toluene	– 78	4	65	< 1
8	**7**	toluene	– 78	4	61	< 1
9	**8**	toluene	– 78	12	30	3
10	**9**	ether	– 78	2	61	< 1
11	**9**	toluene	– 78	4	45	< 1
12	**10**	toluene	– 78	4	32	< 1
13	**12**	ether	– 30[c])	24	16	< 1
14	**12**	toluene	– 30[c])	17	6	< 1
15	**14**	THF	– 78	4	48	16
16	**14**	ether	– 78	12	39	20
17	**14**	toluene	– 78	4	11	31

[a]) All the reactions were conducted with 2 equiv. diaziridine **2** and BuLi. [b]) Isolated yields of corresponding *trans*- and *cis*-aziridinecarboxamides after silica-gel column chromatography. [c]) The reaction was conducted at – 30°. No aziridination occurred at – 78°.

Asymmetric Aziridination of *α,β*-Unsaturated Amides (*Table 3*). – In general, the configuration at the N-atom of trialkylamine ($NR^1R^2R^3$) is invertible at room temperature, and it is impossible to isolate it in an optically active form. However, inversion of the N-atom in a three-membered ring system becomes remarkably slow. Actually, some aziridines and diaziridines have been isolated in optically active forms [8]. As discussed above, the N-atom introduced at C(β) of the α,β-unsaturated amide is chiral. This suggested that asymmetric aziridination would be realized if an optically active diaziridine were used. Thus, optically active diaziridines **15** and **16**/**16**′ were prepared with (1*R*)-1-phenylethylamine as the chiral amine source. The configuration of **15** was assigned by *Kostyanovsky* and co-workers [9]. The relative configuration between N(1) and the benzylic C-atom in the major diastereoisomer **16** was tentatively assigned as depicted, according to [9]. The substituents at N(1) and C(3) were considered to be *trans* to each other for steric reasons. The diastereoisomer ratio of **16**/**16**′ was 7:3 after column chromatography. While **15** gradually isomerized to its diastereoisomer at room temperature, **16** was found to be stable, and no isomerization to the diastereoisomer (**16**′) was detected even after 8 h at 55° in $CDCl_3$[3]). The presence of the *cis*-methyl group in **15** probably facilitates the isomerization.

The results of aziridination with **15** or **16** are summarized in *Table 3*. Aziridination of **3** with *N*-lithiated **15** afforded *cis*-aziridine of > 99% ee as a single product, though the yield was poor (*Entry 1*). Unfortunately, all attempts to increase the yield were

[3]) The isomerization was traced by H-NMR measurements.



15 **16** **16'**

Table 3. *Asymmetric Aziridination of α,β-Unsaturated Amides with Optically Active Diaziridines*[a])

Entry	Substrate	Diaziridine	Solvent	Temp. [°]	Time [h]	Yield [%] (ee [%][b])	
						trans	*cis*
1	**3**	**15**	THF	−30	11	–	4 (>99)[d])
2	**3**	**16**	THF	−78 to −30	4	77 (94)	5 (98)
3	**3**	**16**	THF[c])	−78 to −30	4	–	–
4	**3**	**16**	ether	−78	4	56 (96)	3 (–)
5	**3**	**16**	toluene	−78 to −30	12	76 (98)[e])	3 (>99)[f])
6	**3**	**16'**	toluene	−78 to −30	4	54 (96)[g])	7 (>99)[d])
7	**4**	**16**	toluene	−78 to −30	4	70 (96)	3 (99)
8	**5**	**16**	toluene	−78 to −30	4	80 (96)	6 (>99)
9	**6**	**16**	toluene	−78 to −30	4	76 (96)	3 (99)
10	**7**	**16**	toluene	−78 to −30	4	69 (97)	<1 (–)
11	**8**	**16**	toluene	−78 to −30	4	47 (96)	3 (–)
12	**9**	**16**	ether	−30	4	32 (84)	<1 (–)
13	**9**	**16**	toluene	−78 to −30	12	40 (92)	1 (–)
14	**10**	**16**	toluene	−78 to −30	2	16 (90)	<1 (–)
15	**11**	**16**	toluene	−78 to −30		3 (82)	
16	**13**	**16**	toluene	−78 to −30	4	4 (87)	
17	**14**	**16**	THF	−78 to −30	4	48 (92)[e])	8 (96)[f])
18	**14**	**16**	toluene	−78 to −30	4	39 (95)[e])	31 (88)[f])

[a]) All the reactions were conducted with 2 equiv. of diaziridine and BuLi. [b]) Isolated yields of corresponding *trans*- and *cis*-aziridinecarboxamides after silica-gel column chromatography. Enantiomer excesses (ee) are shown in parentheses. [c]) Dimethylformamide (3 equiv.) was added. [d]) The absolute configuration was (2*R*,3*R*). [e]) The absolute configuration was (2*S*,3*R*). [f]) The absolute configuration was (2*S*,3*S*). [g]) The absolute configuration was (2*R*,3*S*).

fruitless. On the other hand, the reaction with **16** was found to proceed smoothly with high *trans*-selectivity in a highly enantioselective manner. Namely, *trans*-aziridine of 98% ee was obtained as the major isomer in 76% yield from **3** (*Entry 5*). The minor *cis*-aziridine was isolated in only 3%, and its ee was also greater than 99%. The absolute configurations of the products were determined to be (2*S*,3*S*) for the *cis*-isomer and (2*S*,3*R*) for the *trans*-isomer by chemical correlation as described in *Scheme 3*[4]). This result suggested that these diastereoisomers did not come from the common enolate intermediate. Namely, the diastereoselectivity of the first 1,4-addition was reflected in the ratio of *cis*- and *trans*-isomers (*vide infra*).

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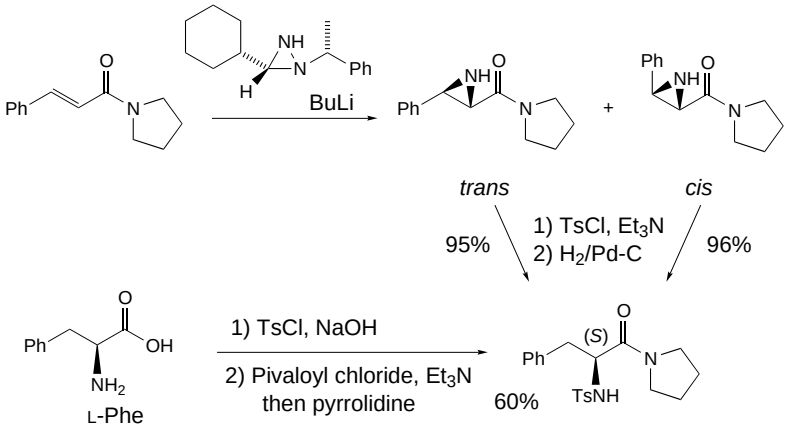
[4]) The retention time t_R of the sample prepared from each aziridinecarboxamide was identical to that of prepared from L-phenylalanine by HPLC with a chiral stationary-phase column (*Daicel Chiralcel OD-H*, hexane ^{i}PrOH 9:1, flow rate 0.5 ml/min): t_R 18.9 min for the (*S*)-form and 22.3 min for the (*R*)-form.

Scheme 3. *Chemical Correlation of Aziridine Derivatives*



Diaziridine **16′** is the diastereoisomer of **16**. However, it behaved as the enantiomer of **16** in the aziridination of **3**. Namely, the reaction with **16′** afforded (2*R*,3*S*)-aziridine (*trans*) in 96% ee (*Entry 6*). The absolute configuration of the aziridine suggested that the configuration of the diaziridine moiety mainly dictated the sense of asymmetric induction in the aziridination, and the chiral N^1 substituent, the (1*R*)-1-phenylethyl group, did not play an important role in the asymmetric induction.

Mechanistic Consideration for the Stereoselectivity. – The stereochemistry of an asymmetric reaction and the solvent effect on the stereochemistry are good probes for the inspection of the reaction mechanism. Therefore, we carefully analyzed the stereochemistry of the present aziridination reactions of **3** with *N*-lithiated **16** in toluene and THF. *N*-Lithiated **16** can adopt the two equilibrating structures Li-**16*α*** and Li-**16*β*** shown in *Fig. 1*, whose lithiated N-atom attacks C(β) of α,β-unsaturated amides. Considering 1,2-chelation, Li-**16*α*** is more favorable than Li-**16*β***. Accordingly, 1,4-addition of the more stable Li-**16*α*** to α,β-unsaturated amides is considered to be a major path. *Fig. 2* explains the stereoselectivity observed for the aziridination of **3** by *N*-lithiated **16** (for convenience, substituents at the diaziridine and the α,β-unsaturated amide are represented by straight lines). The distributions of the stereoisomers in the aziridination in toluene and THF are given at the right side of *Fig. 2*. For the 1,4-addition reaction of *N*-lithiated **16**, there are four possible transition-state conformations **A** – **D** leading to diastereoisomeric enolate intermediates **a1** – **d1**, respectively. By the lack of 1,2-chelation depicted for Li-**16*α*** in *Fig. 1*, **C** and **D** are considered to be less favorable, as compared with **A** and **B**. The observed configurations of the products suggested that the attack of Li-**16*α*** from the *Re*-face of the olefin (**A** in *Fig. 2*) provides enolate **a1** in which the N–N bond and the enolate are suitably aligned for cyclization: the antibonding orbital of the N–N bond can interact with the π-orbital of the amide enolate in *this* conformation. Thus, the reaction proceeds preferentially *via* the enolate intermediate **a1** to give *trans*-(3*R*)-aziridine. On the other hand, the addition of Li-**16*α*** from the *Si*-face is disfavored by the steric interaction between the N-substituent and the β-substituent of the amide (see **B**). Minor intermediate **b1** cyclizes to *cis*-(3*S*)-

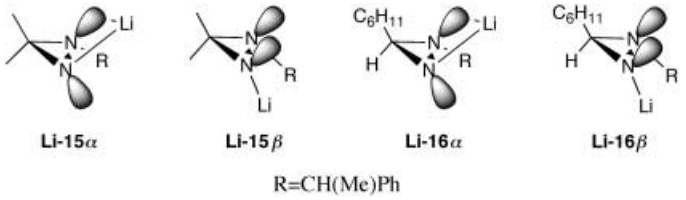


Fig. 1. *Structure of lithiated diaziridine*

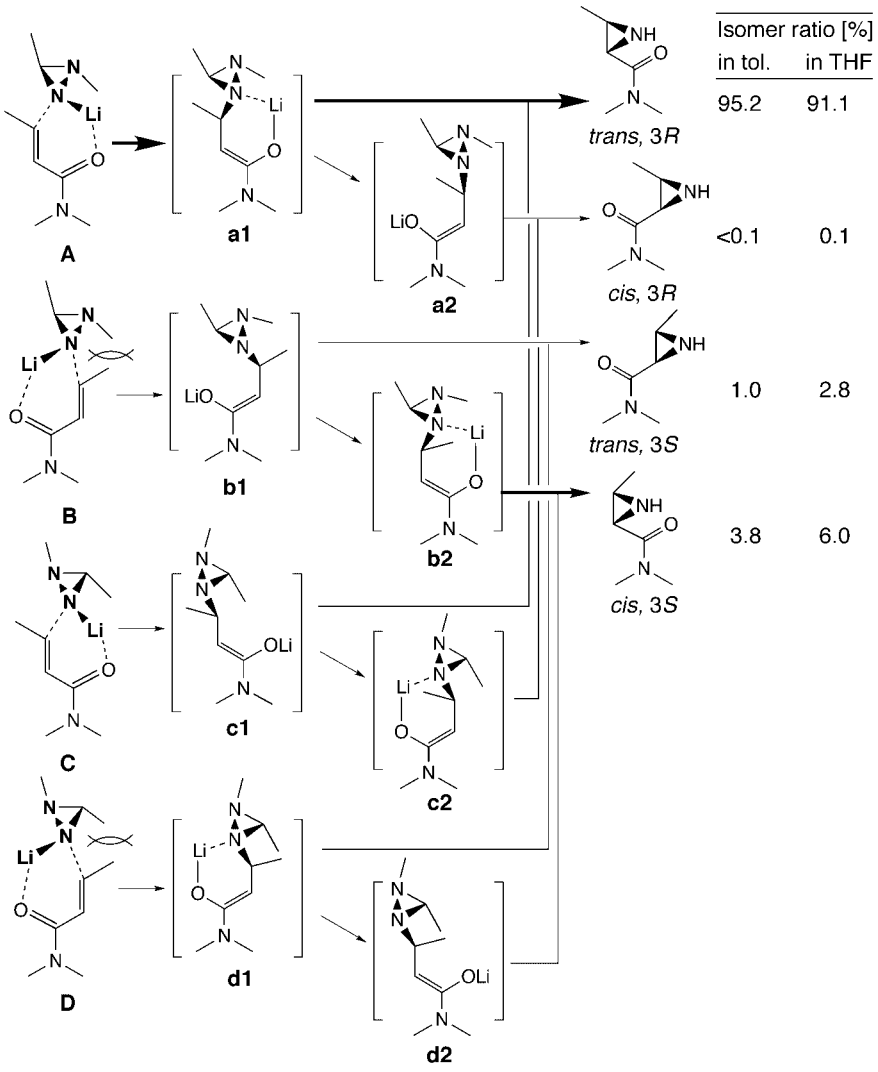


Fig. 2. *Proposed reaction mechanism for asymmetric* trans*-selective aziridination of* trans*-α,β-unsaturated amides with optically active 3-monoalkyldiaziridine*. For convenience, substituents at the diaziridine and the α,β-unsaturated amide are represented by straight lines.

aziridine under rotation of the C(2)–C(3) bond. Use of the polar THF solvent facilitates the dissociation of the coordinating carbonyl group and, therefore, the rotation of the C–C bond to form the minor *cis*-(3*S*)-aziridine, lowering diastereoselectivity. Addition of 3 equiv. dimethylformamide that should coordinate to lithium ion retards the aziridination (*Entry 3* in *Table 3*). This suggests that coordination of the N(2) atom to the lithium ion is indispensable for the cleavage of the N–N bond necessary for aziridination.

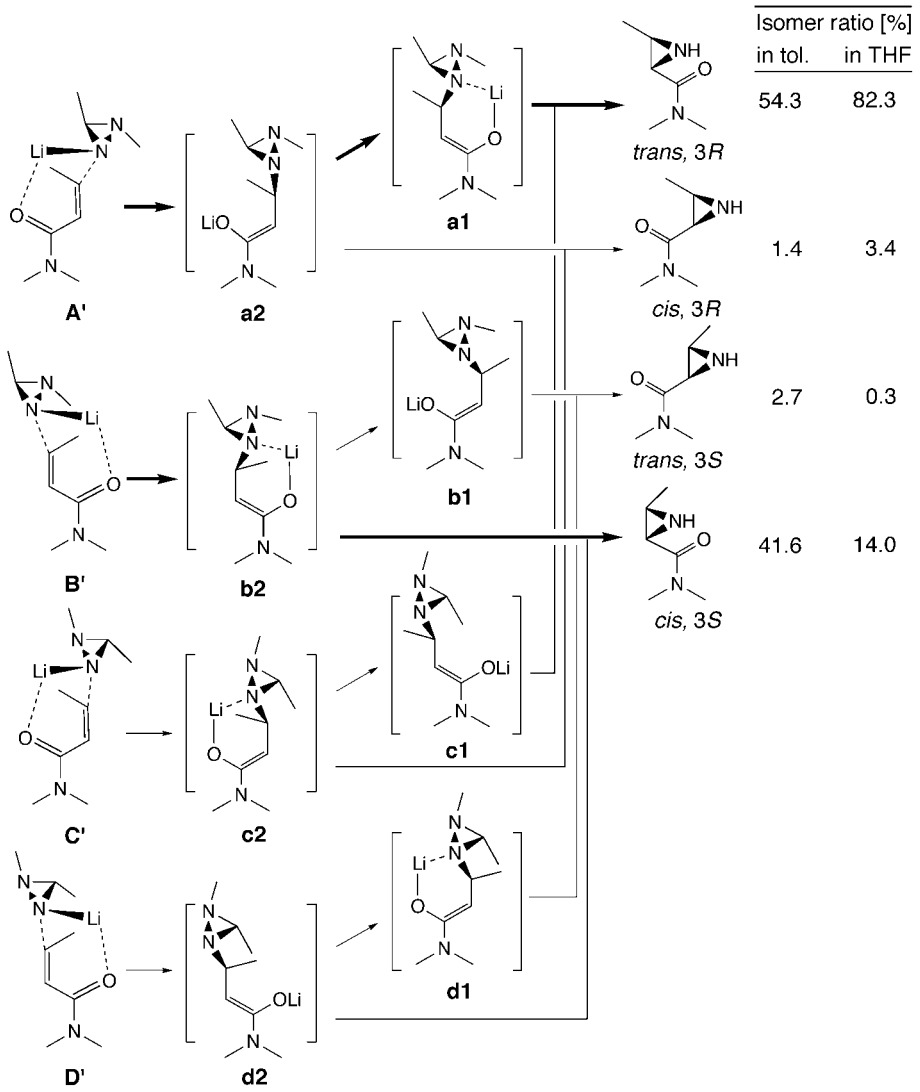


Fig. 3. *Proposed reaction mechanism for asymmetric* trans*-selective aziridination of* cis*-α,β-unsaturated amides with optically active 3-monoalkyldiaziridine.* For convenience, substituents at the diaziridine and the α,β-unsaturated amide are represented by straight lines.

We also inspected the aziridination of *cis*-cinnamamide **14** in toluene (*Fig. 3*). For the same diastereoselection in the addition step as in the reaction of **3**, transition-state conformation **A**′ is considered to be the most favorable, but **B**′ leading to the chelated intermediate **b2** is favored by chelate formation. Thus, in toluene, *cis*-aziridine is produced in considerable amounts. In THF, 1,2-chelation in Li-**16*α*** is interrupted by coordination of THF and thus, *via* sterically favored **A**′, the formation of *trans*-(3*R*)-aziridine is preferred.

Aziridination of **3** with optically active *N*-lithio-3,3-dialkyldiaziridine Li-**15*α*** suffers severe steric repulsion between the alkyl group at C(3) or the substituent at the N-atom and the *β*-substituent of the amide as shown by **A**″, **B**″, and **D**″ in *Fig. 4*. Accordingly, intrinsically low reactive and minor Li-**15*β*** participates as **C**″ and gives the corresponding *cis*-aziridines in low yield, albeit with excellent enantioselectivity.

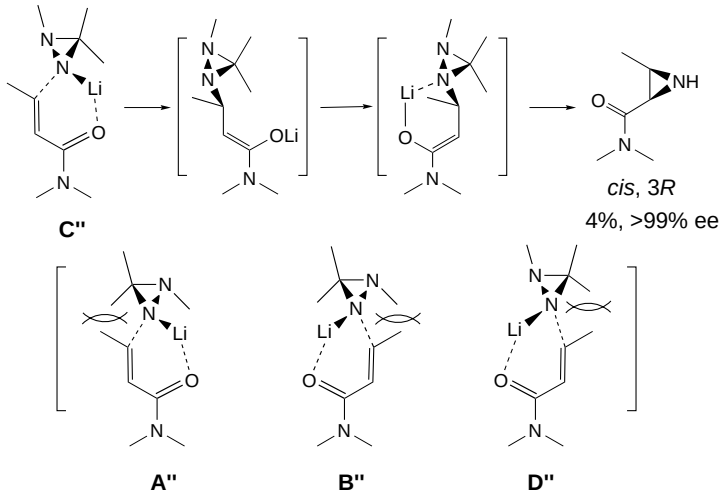


Fig. 4. *Proposed reaction mechanism for asymmetric* cis*-selective aziridination with optically active 3,3-dimethyldiaziridine.* For convenience, substituents at the diaziridine and the *α*,*β*-unsaturated amide are represented by straight lines.

Conclusions. – All of the stereoisomers of *N*-unsubstituted aziridinecarboxamides became available when suitably designed diaziridines were used. Namely, the reaction with 3-monosubstituted diaziridines is *trans*-selective and that with a 3,3-disubstituted diaziridine is *cis*-selective. With optically active diaziridines, highly asymmetric induction as well as diastereoselectivity was achieved. Through the analysis of the stereochemistry and solvent effect, we were able to clarify the factors controlling the stereochemical course of the present aziridination. It is worth noting that the diastereoisomer ratio of the aziridines was largely dependent on the diastereoselectivity in the 1,4-addition of the *N*-lithiated diaziridine to the *α*,*β*-unsaturated amides. These new findings open a new approach to stereoselective synthesis of *N*-unprotected aziridine derivatives and show the potential of diaziridine as an N-donor.

Experimental Part

1. *General*. THF and Et_2O were dried and freshly distilled before use. Dehydrated toluene was from *Kanto Chemical Co., Inc.* Reactions were carried out under N_2 if necessary. Column chromatography (CC): silica gel *60N* (spherical, neutral) from *Kanto Chemical Co*., *Inc*., or basic silica gel *NH* (100–200 mesh) from *Fuji Silysia Chemical Ltd*. HPLC: *Shimadzu Class-VP* equipped with chiral stationary phase column, *Daicel Chiralcel OD-H*; t_R in min. M.p.: uncorrected. $[\alpha]_D$: *Jasco P-1020-GT* automatic digital polarimeter. IR Spectra: *Shimadzu FTIR-8400* instrument; in cm^{-1}. NMR Spectra: *Jeol AL400* instrument; at 400 MHz; δ in ppm downfield from $SiMe_4$ as internal standard, *J* in Hz.

2. *Diaziridines. 3-Cyclohexyl-1-[(1*R*)-1-phenylethyl]diaziridine* (**16**/**16**′). (1*R*)-1-Phenylethylamine (1.29 ml, 10 mmol) was mixed with cyclohexanecarboxaldehyde (1.21 ml, 10 mmol) at r.t. After stirring for 1 h, EtOH (11 ml) and Et_3N (5.3 ml) were added, and the mixture was cooled to 0°. Then, hydroxylamine-*O*-sulfonic acid (1.70 g, 15 mmol) was added to the mixture slowly. After stirring for 30 min at 0°, the mixture was diluted with Et_2O (150 ml). The Et_2O soln. was washed with H_2O, dried ($MgSO_4$), and evaporated and the residue purified by CC (SiO_2, hexane/AcOEt 9:1 → 4:1): **16** (1.55 g, 68%) as colorless crystals and **16**′ (0.589 g, 26%) as a colorless oil. By analogy to the diastereoselectivity reported for the preparation of **15** and its diastereoisomer [9], **16** and **16**′ were expected to have (1*R*,2*R*,3*S*)- and (1*S*,2*S*,3*R*)-configuration respectively.

Data of **16**: M.p. 53.5–55.0°. $[\alpha]_D^{21} = +14.5$ ($c = 1.10$, EtOH). IR (KBr): 532, 698, 737, 843, 926, 1111, 1225, 1277, 1362, 1447, 1495, 2853, 2920, 3036, 3188. ^{1}H-NMR ($CDCl_3$): 7.38–7.21 (*m*, 5 H); 2.66 (*q*, *J* = 6.6, 1 H); 2.33 (*dd*, *J* = 7.3, 7.1, 1 H); 1.89 (*d*, *J* = 7.3, 1 H); 1.72–1.41 (*m*, 4 H); 1.51 (*d*, *J* = 6.6, 3 H); 1.38–1.22 (*m*, 1 H); 1.20–0.85 (*m*, 5 H); 0.77–0.65 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 142.27: 128.19; 127.29; 127.19; 70.23; 64.21; 42.71; 29.18; 28.93; 26.25; 25.54; 25.40; 21.89. Anal. calc. for $C_{15}H_{22}N_2$: C 78.21, H 9.63, N 12.16; found: C 78.05, H 9.59, N 12.14.

Data of **16**′: $[\alpha]_D^{21} = -59.5$ ($c = 1.05$, EtOH). IR (KBr): 567, 698, 760, 849, 924, 1009, 1122, 1205, 1283, 1356, 1448, 1495, 2853, 2926, 3031, 3200. ^{1}H-NMR ($CDCl_3$): 7.41 (*d*, *J* = 7.5, 2 H); 7.33 (*t*, *J* = 7.5, 2 H); 7.24 (*t*, *J* = 7.5, 1 H); 2.73 (*q*, *J* = 6.6, 1 H); 2.41 (*t*, *J* = 7.3, 1 H); 1.72 (*m*, 5 H); 1.38 (*d*, *J* = 6.6, 3 H); 1.31–1.14 (*m*, 5 H); 1.07 (br., 1 H). ^{13}C-NMR ($CDCl_3$): 143.50; 127.92; 126.72; 126.69; 68.85; 64.96; 42.61; 29.52; 29.01; 26.21; 25.47; 25.37; 20.55.

1,2-Diazaspiro[2.5]octane (**1**) [5a]. Colorless crystals. M.p. 104.0–105.0°. IR (KBr): 430, 837, 891, 1045, 1109, 1140, 1219, 1315, 1367, 1406, 1445, 2245, 2598, 2853, 2930, 3163. ^{1}H-NMR ($CDCl_3$): 1.84–1.30 (*m*, 12 H). ^{13}C-NMR ($CDCl_3$): 57.81; 36.41; 25.24; 25.09. Anal. calc. for $C_6H_{12}N_2$: C 64.24, H 10.78, N 24.97; found: C 64.16, H 10.78, N 24.97.

*(1*R*,2*R*)-3,3-Dimethyl-1-[(1*R*)-1-phenylethyl]diaziridines* (**15**). Colorless oil. $[\alpha]_D^{24} = +3.3$ ($c = 1.73$, EtOH). IR (KBr): 557, 606, 702, 758, 1069, 1132, 1238, 1304, 1385, 1452, 1493, 1603, 2928, 2972, 3213. ^{1}H-NMR ($CDCl_3$): 7.38–7.27 (*m*, 4 H); 7.26–7.18 (*m*, 1 H); 3.31 (*t*, *J* = 6.4, 1 H); 1.97 (br. 1 H); 1.47 (*d*, *J* = 6.4, 3 H); 1.38 (*s*, 3 H); 1.21 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 144.15; 128.19; 126.60; 126.31; 62.19; 58.09; 28.45; 24.11; 17.74.

3. *α,β-Unsaturated Amides. 1-[(2*E*)-3-Phenylprop-2-enoyl]pyrrolidine* (**3**). Pyrrolidine (0.4 ml, 4.8 mmol) and Et_3N (0.84 ml, 6.0 mmol) were added to a soln. of cinnamoyl chloride (0.67 g, 4.0 mmol) and *N,N*-dimethylpyridin-4-amine (DMAP; 50 mg, 0.4 mmol) in CH_2Cl_2 (10 ml) at 0°. After stirring for 12 h, the mixture was diluted with H_2O. Extraction with AcOEt, washing with brine, drying, evaporation, and CC (SiO_2, hexane/AcOEt 7:3 → 2:2) afforded **3** (0.77 g, 96%). Colorless crystals. M.p. 99.5–100.0°. IR (KBr): 490, 548, 569, 685, 706, 764, 866, 988, 1196, 1256, 1429, 1451, 1597, 1651, 2876, 2968, 3032, 3059. ^{1}H-NMR ($CDCl_3$): 7.70 (*d*, *J* = 15.6, 1 H); 7.58–7.49 (*m*, 2 H); 7.42–7.31 (*m*, 3 H); 6.80 (*d*, *J* = 15.6, 1 H); 3.62 (*m*, 4 H); 2.07–1.96 (*m*, 2 H); 1.96–1.85 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 164.47; 141.51; 135.23; 129.35; 128.61; 127.68; 118.77; 46.67; 46.13; 26.29; 24.49.

*1-[(2*E*)-But-2-enoyl]pyrrolidine* (**9**). Colorless oil. IR (KBr): 532, 827, 862, 914, 968, 1192, 1308, 1340, 1448, 1604, 1665, 2876, 2970. ^{1}H-NMR ($CDCl_3$): 6.92 (*dq*, *J* = 7.0, 15.1, 1 H); 6.13 (*d*, *J* = 15.1, 1 H); 3.56–3.46 (*m*, 4 H); 2.01–1.91 (*m*, 2 H); 1.91–1.81 (*m*, 2 H); 1.88 (*d*, *J* = 7.0, 3 H). ^{13}C-NMR ($CDCl_3$): 165.40; 141.17; 123.61; 46.71; 45.97; 26.33; 24.52; 18.23.

*(2*E*)-*N*,*N*-Dimethylbut-2-enamide* (**10**). Colorless oil. IR (KBr): 496, 631, 831, 968, 1101, 1159, 1258, 1402, 1448, 1499, 1609, 1661, 2939. ^{1}H-NMR ($CDCl_3$): 6.87 (*dq*, *J* = 7.0, 15.1, 1 H); 6.27 (*dq*, *J* = 1.5, 15.1, 1 H); 3.07 (*s*, 3 H); 3.00 (*s*, 3 H); 1.88 (*dd*, *J* = 1.5, 7.0, 3 H). ^{13}C-NMR ($CDCl_3$): 166.59; 140.94; 121.62; 37.37; 35.69; 18.28.

*1-[(2*E*)-3-(4-Methoxyphenyl)prop-2-enoyl]pyrrolidine* (**4**). A soln. of 4-methoxycinnamic acid (0.89 g, 5 mmol) in THF (35 ml) was cooled to −15°, and Et_3N (0.70 ml, 5 mmol) and pivaloyl chloride (0.62 ml, 5 mmol) were added. After stirring for 5 min, pyrrolidine (0.42 ml, 5 mmol) was added at −15°, and the mixture

was stirred for 20 min, then allowed to warm to r.t., stirred for 15 min, concentrated, dissolved in AcOEt, and washed with 5% $NaHCO_3$ soln., H_2O, 1N HCl, and H_2O. Column chromatography (SiO_2, hexane/AcOEt 1:1 → 3:7) afforded **4** (0.90 g, 62%). Colorless crystals. M.p. 115.0–115.5°. IR (KBr): 820, 984, 1018, 1175, 1248, 1304, 1431, 1510, 1597, 1643, 2841, 2874, 2957, 3059. ^{1}H-NMR ($CDCl_3$): 7.66 (*d*, *J* = 15.3, 1 H); 7.48 (*d*, *J* = 8.5, 2 H); 6.89 (*d*, *J* = 8.5, 2 H); 6.61 (*d*, *J* = 15.3, 1 H); 3.83 (*s*, 3 H); 3.66–3.55 (*m*, 4 H); 2.06–1.95 (*m*, 2 H); 1.95–1.84 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 165.66; 161.38; 141.87; 129.89; 128.63; 116.97; 114.67; 55.68; 46.86; 46.32; 26.43; 24.64.

*1-[(2*E*)-3-(4-Chlorophenyl)prop-2-enoyl]pyrrolidine* (**5**). Colorless crystals. M.p. 154.0–154.5°. IR (KBr): 496, 976, 1086, 1398, 1429, 1489, 1605, 1651, 2872, 2966. ^{1}H-NMR ($CDCl_3$): 7.65 (*d*, *J* = 15.6, 1 H); 7.46 (*d*, *J* = 8.5, 2 H); 6.71 (*d*, *J* = 15.6, 1 H); 3.61 (*m*, 4 H); 2.08–1.97 (*m*, 2 H); 1.96–1.85 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 165.02; 140.88; 135.86; 134.39; 129.53; 119.89; 46.92; 46.41; 26.42; 24.60.

*1-[(2*E*)-3-(1-Naphthyl)prop-2-enoyl]pyrrolidine* (**6**). Pyrrolidine (13.1 ml, 159 mmol) and Et_3N (22.0 ml, 159 mmol) were added to a soln. of bromoacetyl chloride (25.0 g, 159 mmol) in CH_2Cl_2 (500 ml) at 0°. After stirring for 2 h, the mixture was diluted with H_2O. The org. layer was washed with 1N HCl and H_2O and dried. Evaporation afforded 1-(bromoacetyl)pyrrolidine (18.3 g, 60%) as colorless crystals. A part of this sample (3.33 g, 17.3 mmol) was mixed with triethyl phosphite (3.56 ml, 20.8 mmol) and refluxed for 3.5 h at 180°. CC (SiO_2, CH_2Cl_2/MeOH 33:1) afforded the corresponding phosphonate in quant. yield. Na OMe (366 mg, 6.8 mmol) was added to the phosphonate (1.0 g, 4.0 mmol) at 0°. The mixture was stirred for 40 min, and 1-naphthaldehyde (2.58 ml, 4.4 mmol) was added at 0°. After stirring at r.t. for 3 h, the mixture was diluted with AcOEt and H_2O. Extraction and CC afforded **6** (0.91 g, 91%). Colorless crystals. M.p. 131.0–132.5°. IR (KBr): 422, 553, 596, 706, 746, 783, 814, 1003, 1169, 1348, 1429, 1599, 1641, 2872, 2941, 2976, 3047. ^{1}H-NMR ($CDCl_3$): 8.52 (*d*, *J* = 15.1, 1 H); 8.25 (*d*, *J* = 8.5, 1 H); 7.87 (*d*, *J* = 8.0, 2 H); 7.72 (*d*, *J* = 7.5, 1 H); 7.60–7.43 (*m*, 3 H); 6.80 (*d*, *J* = 15.1, 1 H); 3.70–3.61 (*m*, 4 H); 2.08–1.98 (*m*, 2 H); 1.98–1.88 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 164.36; 138.84; 133.49; 133.02; 131.40; 129.55; 128.39; 126.49; 125.99; 125.22; 124.40; 123.74; 121.88; 46.72; 46.16; 26.30; 24.50.

*1-[(2*E*)-3-(2-Furyl)prop-2-enoyl]pyrrolidine* (**7**). Colorless crystals. M.p. 100.5–101.5°. IR (KBr): 762, 988, 1030, 1479, 1552, 1597, 1655, 2880, 2972, 3088, 3134. ^{1}H-NMR ($CDCl_3$): 7.46 (*d*, *J* = 15.6, 1 H); 7.44 (*s*, 1 H); 6.64 (*d*, *J* = 15.6, 1 H); 6.54 (*d*, *J* = 3.1, 1 H); 6.45 (*dd*, *J* = 2.0, 3.5, 1 H); 3.60 (*m*, 4 H); 2.05–1.95 (*m*, 2 H); 1.95–1.85 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 164.38; 151.59; 143.56; 128.19; 116.51; 113.54; 112.00; 46.63; 46.07; 26.23; 24.50.

*1-[(2*E*)-5-Methylhexa-2,4-dienoyl]pyrrolidine* (**8**). Colorless crystals. M.p. 101.0–102.0°. IR (KBr): 571, 710, 883, 991, 1045, 1196, 1254, 1315, 1340, 1420, 1583, 1645, 2874, 2968. ^{1}H-NMR ($CDCl_3$): 7.57 (*dd*, *J* = 11.5, 14.7, 1 H); 6.06 (*d*, *J* = 14.7, 1 H); 6.00 (*d*, *J* = 11.5, 1 H); 3.58–3.48 (*m*, 4 H); 2.02–1.92 (*m*, 2 H); 1.92–1.82 (*m*, 2 H); 1.89 (*s*, 3 H); 1.86 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 166.16; 144.94; 138.70; 124.56; 119.86; 46.73; 46.15; 26.75; 26.38; 24.60; 19.11.

N,N-*Dimethylprop-2-enamide* (**11**). Colorless oil. IR (KBr): 797, 981, 1055, 1155, 1259, 1423, 1499, 1603, 1647, 2940. ^{1}H-NMR ($CDCl_3$): 6.59 (*dd*, *J* = 10.5, 17.1, 1 H); 6.30 (*dd*, *J* = 2.0, 17.1, 1 H); 5.67 (*dd*, *J* = 2.0, 10.5, 1 H); 3.09 (*s*, 3 H); 3.02 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 166.32; 127.50; 127.36; 37.41; 35.70.

*1-[(2*E*)-2-Methylbut-2-enoyl]pyrrolidine* (**12**). Colorless oil. IR (KBr): 648, 1165, 1437, 1609, 2878, 2972. ^{1}H-NMR ($CDCl_3$): 5.79–5.70 (*m*, 1 H); 3.55–3.36 (*m*, 4 H); 1.87 (*m*, 4 H); 1.84 (*s*, 3 H); 1.70 (*d*, *J* = 17.5, 3 H). ^{13}C-NMR ($CDCl_3$): 171.76; 133.39; 126.20; 48.74; 45.60; 26.28; 24.51; 13.65; 13.39.

1-(3-Methylbut-2-enoyl)pyrrolidine (**13**). Colorless oil. IR (KBr): 529, 841, 1192, 1340, 1373, 1452, 1609, 1655, 2876, 2972. ^{1}H-NMR ($CDCl_3$): 5.79 (*m*, 1 H); 3.53–3.46 (*m*, 2 H); 3.46–3.39 (*m*, 2 H); 2.08 (*d*, *J* = 1.5, 3 H); 1.98–1.81 (*m*, 4 H); 1.86 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 166.00; 148.36; 117.83; 46.82; 46.65; 45.25; 26.93; 26.18; 24.41; 20.07.

*1-[(2*Z*)-3-Phenylprop-2-enoyl]pyrrolidine* (**14**). Thionyl chloride (6.51 ml, 89 mmol) was mixed with phenylprop-2-ynoic acid (0.26 g, 1.79 mmol), and the mixture was heated at 50° for 6 h. After evaporation, the mixture was diluted with CH_2Cl_2 (10 ml), pyrrolidine (0.15 ml, 1.79 mmol), and Et_3N (0.25 ml, 1.79 mmol). Extraction and CC (SiO_2, hexane/AcOEt 7:3 → 2:3) afforded *N*-[phenylprop-2-ynoyl]pyrrolidine (0.26 g, 74%). Two drops of *tert*-amyl alcohol (= 2-methylbutan-2-ol), quinoline (0.53 ml) and 10% Pd/C (5.6 mg) were added to the amide, and the mixture was cooled to −40°, then stirred for 3 days under 1 atm of H_2. Filtration and CC (SiO_2, hexane/AcOEt 3:2 → 3:7) afforded **14** (0.20 g, 74%). Colorless oil. IR (KBr): 698, 779, 1377, 1441, 1609, 2876, 2970, 3023, 3057. ^{1}H-NMR ($CDCl_3$): 7.46–7.39 (*m*, 2 H); 7.35–7.24 (*m*, 3 H); 6.64 (*d*, *J* = 12.6, 1 H); 6.06 (*d*, *J* = 12.6, 1 H); 3.57–3.46 (*m*, 2 H); 3.24–3.14 (*m*, 2 H); 1.86–1.69 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 166.85; 135.44; 133.35; 128.27; 128.24; 128.12; 124.05; 46.96; 45.33; 25.86; 24.38.

4. *Typical Procedure for* cis-*Selective Aziridination*. A soln. of 1.6M BuLi in hexane (0.254 ml, 0.40 mmol) was added to a soln. of **1** (45 mg, 0.40 mmol) in THF (4 ml) at −78°. A THF soln. of **3** (40 mg, 0.20 mmol) was

added to the mixture at −78°, and the mixture allowed to warm to −30°. After stirring for 11 h at −30°, the mixture was diluted with H_2O. Extraction with CH_2Cl_2 and CC (basic silica gel, hexane/AcOEt 4:1 → 3:2) afforded 2,3-*cis*-aziridinecarboxamide as colorless crystals (42 mg, 97%). NMR: identical to those of the optically active sample prepared by asymmetric aziridination (*vide infra*).

N,N-*Dimethylaziridinecarboxamide* (from **11**). Colorless oil. IR (KBr): 486, 606, 847, 1007, 1153, 1242, 1352, 1427, 1508, 1632, 2943, 3271. ^{1}H-NMR ($CDCl_3$): 3.19 (*s*, 3 H); 3.01 (*s*, 3 H); 2.68 (*dd*, *J* = 3.0, 5.0, 1 H); 1.85–1.78 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 170.51; 36.52; 36.13; 27.86; 26.69.

*1-{[(2*R*,3*R*)-2,3-Dimethylaziridin-2-yl]carbonyl}pyrrolidine* (from **12**). Colorless oil. IR (KBr): 623, 824, 897, 1065, 1190, 1277, 1344, 1450, 1616, 2882, 2972, 3275. ^{1}H-NMR ($CDCl_3$): 3.68–3.39 (*m*, 4 H); 2.10–1.74 (*m*, 6 H); 1.46 (*s*, 3 H); 1.14 (*d*, *J* = 6.0, 3 H). ^{13}C-NMR ($CDCl_3$): 169.74; 47.15; 46.09; 42.62; 38.86; 26.58; 24.00; 20.67; 15.60.

1-[(3,3-Dimethylaziridin-2-yl)carbonyl]pyrrolidine (from **13**). Colorless oil. IR (KBr): 530, 664, 816, 858, 907, 1105, 1188, 1310, 1381, 1460, 1628, 2880, 2963, 3269. ^{1}H-NMR ($CDCl_3$): 3.63–3.41 (*m*, 4 H); 2.41 (*s*, 1 H); 2.11–1.79 (*m*, 4 H); 1.30 (*s*, 3 H); 1.24 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 167.17; 46.12; 45.89; 43.59; 38.38; 26.02; 24.30; 21.61; 19.02.

5. *Typical Procedure for* trans-*Selective Aziridination*. A soln. of 1.6M BuLi in hexane (0.254 ml, 0.40 mmol) was added to a soln. of **2** (56 mg, 0.40 mmol) in toluene (4 ml) at −78°. A toluene soln. of **3** (40 mg, 0.20 mmol) was added to the mixture. After stirring for 4 h at −78°, the mixture was diluted with H_2O. Extraction with CH_2Cl_2 and CC (basic silica gel, hexane/AcOEt 4:1 → 3:2) afforded *trans*-aziridinecarboxamide as colorless crystals (32 mg, 74%). NMR: identical with those of the optically active sample prepared by asymmetric aziridination (*vide infra*).

*1-{[(2*R*,3*S*)-2,3-Dimethylaziridin-2-yl]carbonyl}pyrrolidine* (from **12**). Colorless oil. IR (KBr): 629, 824, 966, 1067, 1111, 1188, 1259, 1342, 1448, 1620, 2882, 2936, 3281. ^{1}H-NMR ($CDCl_3$): 3.59–3.37 (*m*, 4 H); 2.06 (*q*, *J* = 5.5, 1 H); 2.05–1.67 (*m*, 5 H); 1.40 (*s*, 3 H); 1.22 (*d*, *J* = 5.5, 3 H). ^{13}C-NMR ($CDCl_3$): 172.33; 47.56; 46.52; 40.37; 35.74; 26.42; 24.16; 15.26; 14.29.

6. *Typical Procedure for Asymmetric Aziridination*. A soln. of 1.6M BuLi in hexane (0.254 ml, 0.40 mmol) was added to a soln. of **16** (92 mg, 0.40 mmol) in toluene (4 ml) at −78°. A toluene soln. of **3** (40 mg, 0.20 mmol) was added slowly to the mixture at −78° for 1 h. After stirring for 1 h at −78°, the mixture was allowed to warm to −30°. After stirring for 12 h at −30°, the mixture was diluted with H_2O. Extraction with CH_2Cl_2 and CC (basic silica gel, hexane/AcOEt 4:1 → 2:3) afforded *1-{[(2*S*,3*R*)-3-phenylaziridin-2-yl]carbonyl}pyrrolidine* (33 mg, 76%) as colorless crystals from the more polar fraction. HPLC (*Daicel Chiralcel OD-H*, hexane/^{i}PrOH 9:1, flow rate 0.5 ml/min): 98% ee; t_R 28.3 (major (2*S*,3*R*)-isomer), 42.7 (minor (2*R*,3*S*)-isomer)[5]). M.p. 84.5–85.5°. $[\alpha]_D^{23} = +148.5$ (*c* = 0.50, EtOH). IR (KBr): 540, 588, 694, 754, 799, 856, 1038, 1196, 1331, 1406, 1460, 1624, 2874, 2970, 3034, 3246. ^{1}H-NMR ($CDCl_3$): 7.40–7.19 (*m*, 5 H); 3.64–3.46 (*m*, 4 H); 3.14 (*s*, 1 H); 2.59 (*s*, 1 H); 2.24 (br. 1 H); 2.06–1.81 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 165.34; 135.01; 128.01; 127.28; 126.75; 45.84; 45.75; 39.50; 26.00; 24.18. Anal. calc. for $C_{13}H_{16}N_2O$: C 72.19, H 7.46, N 12.95; found: C 72.17, H 7.49, N 12.74.

From the less polar fraction, *1-{[(2*S*,3*S*)-3-phenylaziridin-2-yl]carbonyl}pyrrolidine* (1.5 mg, 3%) was isolated as colorless crystals. HPLC (*Daicel Chiralcel OD-H* × *2* (2 columns connected in series), hexane/^{i}PrOH 2:1, flow rate 0.5 ml/min): >99% ee; t_R 31.7 (minor (2*R*,3*R*)-isomer), 38.5 (major (2*S*,3*S*)-isomer)[6]). M.p. 132.0–133.0°. $[\alpha]_D^{24} = -79.1$ (*c* = 1.18, EtOH). IR (KBr): 523, 698, 748, 901, 1198, 1360, 1454, 1630, 2876, 2976, 3219. ^{1}H-NMR ($CDCl_3$): 7.35–7.10 (*m*, 5 H); 3.59–3.30 (*m*, 4 H); 3.20–3.11 (*m*, 1 H); 2.96 (br., 1 H); 2.10 (br., 1 H); 2.03–1.65 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 168.44; 139.31; 128.88; 127.93; 126.58; 46.64; 46.37; 40.07; 39.93; 26.10; 24.40. Anal. calc. for $C_{13}H_{16}N_2O$: C 72.19, H 7.46, N 12.95; found: C 72.05, H 7.59, N 12.86.

*1-{[(2*S*,3*R*)-3-(4-Methoxyphenyl)aziridin-2-yl]carbonyl}pyrrolidine* (from **4**). Colorless crystals. M.p. 75.0–77.0°. HPLC: 96% ee. $[\alpha]_D^{26} = +160.0$ (*c* = 1.87, EtOH). IR (KBr): 546, 820, 1032, 1178, 1250, 1306, 1456, 1516, 1632, 2878, 2966, 3261. ^{1}H-NMR ($CDCl_3$): 7.23 (*d*, *J* = 8.5, 2 H); 6.86 (*d*, *J* = 8.5, 2 H); 3.80 (*s*, 3 H); 3.65–3.46 (*m*, 4 H); 3.10 (*s*, 1 H); 2.55 (*s*, 1 H); 2.19 (br., 1 H); 2.08–1.80 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 167.70; 158.83; 130.65; 127.00; 113.72; 55.31; 46.38; 46.13; 39.74; 39.39; 25.97; 24.29. Anal. calc. for $C_{14}H_{18}N_2O_2$: C 68.27, H 7.37, N 11.37; found: C 68.33, H 7.35, N 11.24.

*1-{[(2*S*,3*S*)-3-(4-Methoxyphenyl)aziridin-2-yl]carbonyl}pyrrolidine* (from **4**). Colorless crystals. M.p. 120.0–121.5°. HPLC: 99% ee. IR (KBr): 515, 677, 814, 839, 905, 1030, 1182, 1248, 1360, 1458, 1514, 1636, 2878, 2976, 3221. ^{1}H-NMR ($CDCl_3$): 7.15 (*d*, *J* = 8.5, 2 H); 6.81 (*d*, *J* = 8.5, 2 H); 3.77 (*s*, 3 H); 3.60–3.29

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[5]) The same elution order was observed for the other aziridinecarboxamides prepared form **4**–**10**.

[6]) The same elution order was observed for the other aziridinecarboxamides prepared form **4**–**6**.

(*m*, 4 H); 3.23–3.11 (*m*, 1 H); 2.92 (*d*, *J* = 5.5, 1 H); 2.12–1.66 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 158.64; 127.87; 113.55; 55.24; 45.89; 45.78; 40.11; 39.32; 26.04; 24.26. Anal. calc. for $C_{14}H_{18}N_2O_2$: C 68.27, H 7.37, N 11.37; found: C 68.09, H 7.32, N 11.10.

1-{[(2S,3R)-3-(4-Chlorophenyl)aziridin-2-yl]carbonyl}pyrrolidine (from **5**). Colorless crystals. M.p. 119.0–120.5°. HPLC: 96% ee. $[\alpha]_D^{25} = +150.8$ (*c* = 1.03, EtOH). IR (KBr): 498, 534, 733, 812, 858, 1011, 1034, 1088, 1169, 1192, 1333, 1414, 1458, 1626, 2874, 2972, 3047, 3258. ^{1}H-NMR ($CDCl_3$): 7.31–7.21 (*m*, 4 H); 3.65–3.44 (*m*, 4 H); 3.11 (*s*, 1 H); 2.53 (*s*, 1 H); 2.24 (br., 1 H); 2.07–1.82 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 167.32; 137.24; 133.06; 128.43; 127.32; 46.48; 46.19; 40.02; 39.13; 26.02; 24.32. Anal. calc. for $C_{13}H_{15}ClN_2O$: C 62.28, H 6.03, N 11.17; found: C 62.28, H 6.05, N 11.07.

1-{[(2S,3S)-3-(4-Chlorophenyl)aziridin-2-yl]carbonyl}pyrrolidine (from **5**). Colorless crystals. M.p. 124.0–125.0°. HPLC: > 99% ee. IR (KBr): 519, 808, 858, 903, 1015, 1090, 1186, 1358, 1458, 1638, 2876, 2978, 3221. ^{1}H-NMR ($CDCl_3$): 7.29–7.10 (*m*, 4 H); 3.64–3.26 (*m*, 4 H); 3.24–3.11 (*m*, 1 H); 2.94 (br., 1 H); 2.15–1.56 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 165.91; 133.80; 128.89; 128.86; 46.17; 46.04; 39.59; 26.18; 24.32. Anal. calc. for $C_{13}H_{15}ClN_2O$: C 62.28, H 6.03, N 11.17; found: C 62.46, H 6.07, N 11.08.

1-{[(2R,3S)-3-(1-Naphthyl)aziridin-2-yl]carbonyl}pyrrolidine (from **6**). Colorless crystals. M.p. 126.0–127.0°. HPLC: 96% ee. $[\alpha]_D^{25} = -131.0$ (*c* = 0.50, EtOH). IR (KBr): 422, 515, 615, 773, 802, 851, 1032, 1192, 1261, 1339, 1460, 1630, 2882, 2978, 3058, 3244. ^{1}H-NMR ($CDCl_3$): 7.63 (*dd*, *J* = 2.0, 8.3, 1 H); 7.43 (*dd*, *J* = 2.0, 8.0, 1 H); 7.32 (*d*, *J* = 8.5, 1 H); 7.20 (*d*, *J* = 7.0, 1 H); 7.11–7.02 (*m*, 2 H); 7.04–6.97 (*m*, 1 H); 3.25 (*d*, *J* = 1.5, 1 H); 3.22–3.13 (*m*, 2 H); 3.11–3.02 (*m*, 1 H); 2.13 (*d*, *J* = 2.5, 1 H); 1.84 (br. 1 H); 1.58–1.36 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 168.72; 134.93; 133.89; 132.46; 129.31; 128.25; 126.70; 126.23; 126.15; 124.28; 123.26; 46.75; 46.53; 38.96; 38.13; 26.19; 24.47. Anal. calc. for $C_{17}H_{18}N_2O$: C 76.66, H 6.81, N 10.57; found: C 76.38, H 6.81, N 10.48.

1-{[(2S,3S)-3-(1-Naphthyl)aziridin-2-yl]carbonyl}pyrrolidine (from **6**). Colorless oil. HPLC: 99% ee. IR (KBr): 519, 779, 799, 862, 1190, 1348, 1456, 1634, 2876, 2970, 3246. ^{1}H-NMR ($CDCl_3$): 8.15 (*d*, *J* = 8.5, 1 H); 7.85 (*dd*, *J* = 1.5, 8.3, 1 H); 7.76 (*d*, *J* = 8.0, 1 H); 7.56–7.46 (*m*, 2 H); 7.46–7.40 (*m*, 1 H); 7.33 (*d*, *J* = 7.0, 1 H); 3.81 (*d*, *J* = 5.5, 1 H); 3.72–3.59 (*m*, 2 H); 3.34–3.25 (*m*, 1 H); 3.19 (*d*, 5.5, 1 H); 2.96–2.86 (*m*, 1 H); 2.00–1.40 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 165.20; 133.11; 131.89; 130.89; 128.70; 127.86; 125.68; 125.47; 125.09; 124.36; 122.74; 46.26; 45.95; 39.33; 37.81; 25.95; 24.02.

1-{[(2R,3S)-3-(2-Furyl)aziridin-2-yl]carbonyl}pyrrolidine (from **7**). Colorless crystals. M.p. 69.0–70.5°. HPLC: 97% ee. $[\alpha]_D^{24} = +150.9$ (*c* = 1.33, EtOH). IR (KBr): 525, 677, 752, 804, 858, 932, 1013, 1190, 1229, 1319, 1464, 1626, 2872, 2976, 3109, 3223. ^{1}H-NMR ($CDCl_3$): 7.33 (*d*, *J* = 2.0, 1 H); 6.33 (*dd*, *J* = 2.0, 3.0, 1 H); 6.29 (*d*, *J* = 3.0, 1 H); 3.71–3.46 (*m*, 4 H); 3.16 (*s*, 1 H); 2.92 (*s*, 1 H); 2.14 (br. 1 H); 2.10–1.78 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 167.18; 151.72; 141.75; 110.37; 106.92; 46.44; 46.16; 36.87; 33.76; 25.99; 24.30. Anal. calc. for $C_{11}H_{14}N_2O_2$: C 64.06, H 6.84, N 13.58; found: C 64.26, H 6.90, N 13.51.

1-{[(2S,3S)-3-(2-Furyl)aziridin-2-yl]carbonyl}pyrrolidine (from **7**). Colorless crystals. M.p. 75.0–77.0°. HPLC: > 99% ee. IR (KBr): 408, 455, 509, 598, 679, 706, 756, 820, 854, 989, 1043, 1097, 1159, 1352, 1462, 1638, 2880, 2953, 3117, 3153, 3258. ^{1}H-NMR ($CDCl_3$): 7.31 (*d*, *J* = 2.0, 1 H); 6.29 (*dd*, *J* = 2.0, 3.0, 1 H); 6.15 (*d*, *J* = 3.0, 1 H); 3.60–3.42 (*m*, 3 H); 3.39–3.30 (*m*, 1 H); 3.29 (*s*, 1 H); 2.93 (*s*, 1 H); 2.13–1.76 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 165.27; 149.64; 141.88; 110.41; 106.40; 46.01; 45.83; 38.75; 33.55; 25.95; 24.29. Anal. calc. for $C_{11}H_{14}N_2O_2$: C 64.06, H 6.84, N 13.58; found: C 64.11, H 6.94, N 13.53.

1-{[(2R,3S)-3-(2-Methylprop-1-enyl)aziridin-2-yl]carbonyl}pyrrolidine (from **8**). Colorless oil. HPLC: 96% ee. $[\alpha]_D^{26} = -31.1$ (*c* = 0.42, EtOH). IR (KBr): 496, 802, 856, 1167, 1246, 1342, 1454, 1632, 2878, 2968, 3260. ^{1}H-NMR ($CDCl_3$): 4.81 (*d*, *J* = 8.79, 1 H); 3.68–3.44 (*m*, 4 H); 2.74 (*dd*, *J* = 8.79, 2.44, 1 H); 2.46 (*d*, *J* = 2.44, 1 H); 2.10–1.75 (*m*, 5 H); 1.76 (*s*, 3 H); 1.72 (*s*, 3 H).^{13}C-NMR ($CDCl_3$): 168.36; 137.00; 123.48; 46.38; 46.14; 37.02; 36.34; 26.06; 25.81; 24.35; 18.57.

1-{[(2S,3S)-3-(2-Methylprop-1-enyl)aziridin-2-yl]carbonyl}pyrrolidine (from **8**). Colorless oil. IR (KBr): 419, 521, 692, 737, 806, 870, 1053, 1078, 1123, 1159, 1229, 1346, 1458, 1634, 2880, 2966, 3240. ^{1}H-NMR ($CDCl_3$): 4.89 (*d*, *J* = 9.28,1 H); 3.60–3.45 (*m*, 4 H); 2.87 (*dd*, *J* = 9.28, 5.62, 1 H); 2.79 (*d*, *J* = 5.62, 1 H); 2.10–1.80 (*m*, 5 H); 1.78 (*s*, 3 H); 1.71 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 167.64; 139.22; 119.58; 46.35; 46.17; 37.88; 35.89; 26.23; 26.19; 24.48; 18.57.

1-{[(2R,3S)-3-Methylaziridin-2-yl]carbonyl}pyrrolidine (from **9**). Colorless oil. HPLC: 92% ee. $[\alpha]_D^{22} = +3.3$ (*c* = 0.92, EtOH). IR (KBr): 451, 525, 723, 831, 941, 1090, 1165, 1246, 1323, 1412, 1464, 1628, 2880, 2970, 3269. ^{1}H-NMR ($CDCl_3$): 3.70–3.40 (*m*, 4 H); 2.28 (*d*, *J* = 2.5, 1 H); 2.16 (*dq*, *J* = 2.5, 5.0, 1 H); 2.10–1.78 (*m*, 5 H); 1.24 (*d*, *J* = 5.0, 3 H). ^{13}C-NMR ($CDCl_3$): 168.72; 46.30; 46.15; 36.53; 33.94; 26.08; 24.35; 18.38.

1-{[(2S,3S)-3-Methylaziridin-2-yl]carbonyl}pyrrolidine (from **9**). Colorless oil. IR (KBr): 527, 681, 826, 858, 1009, 1175, 1231, 1350, 1462, 1628, 2880, 2970, 3263. ^{1}H-NMR ($CDCl_3$): 3.63–3.45 (*m*, 4 H); 2.61 (*d*, *J* = 6.0,

1 H); 2.27 (*dq*, *J* = 6.0, 6.0, 1 H); 2.11 – 1.80 (*m*, 5 H); 1.23 (*d*, *J* = 6.0, 3 H). ^{13}C-NMR ($CDCl_3$): 166.92; 46.01; 45.96; 36.04; 32.96; 26.06; 24.28; 13.22.

*(2*R*,3*S*)-*N,N,*3-Trimethylaziridine-2-carboxamide* (from **10**). Colorless oil. HPLC: 90% ee. $[\alpha]_D^{23} = -20.7$ (*c* = 0.42, EtOH). IR (KBr): 496, 621, 833, 941, 1088, 1165, 1252, 1329, 1404, 1435, 1504, 1638, 2934, 3271. ^{1}H-NMR ($CDCl_3$): 3.16 (*s*, 3 H); 3.00 (*s*, 3 H); 2.38 (*s*, 1 H); 2.08 (br., 1 H); 1.69 (br. 1 H); 1.25 (*d*, *J* = 5.5, 3 H). ^{13}C-NMR ($CDCl_3$): 170.27; 36.63; 36.05; 35.45; 33.89; 18.32.

*(2*S*,3*S*)-*N,N,*3-Trimethylaziridine-2-carboxamide* (from **10**). Colorless oil. IR (KBr): 604, 833, 1009, 1105, 1134, 1169, 1261, 1406, 1426, 1504, 1638, 2936, 3269. ^{1}H-NMR ($CDCl_3$): 3.13 (*s*, 3 H); 3.02 (*s*, 3 H); 2.70 (*d*, *J* = 6.0, 1 H); 2.29 (*dq*, *J* = 6.0, 5.5, 1 H); 1.19 (*d*, *J* = 5.5, 3 H). ^{13}C-NMR ($CDCl_3$): 168.53; 36.42; 35.73; 35.62; 32.86; 13.42.

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