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Generation of Aziridinyllithiums from Sulfinylaziridines with *tert*-Butyllithium: Properties, Reactivity, and Application to a Synthesis of α,α-Dialkylamino Acid Esters and Amides Including an Optically Active Form

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Abstract—Aziridinyllithiums were generated from sulfinylaziridines by a sulfoxide–lithium exchange reaction of sulfoxides with *tert*-butyllithium at low temperature. The generated aziridinyllithiums were found to be stable in THF at below −30°C and they are reactive with several electrophiles such as carbonyl compounds, ethyl chloroformate, and phenyl isocyanate. The reactivities of the aziridinyllithiums having several alkyl groups were investigated. As an extension of this method, a synthesis of α,α-dialkylamino acid esters, including an optically active form, and amides was realized via the aziridinyllithiums. *N*-Non substituted α,α-dialkylamino acid esters were synthesized starting from *N*-(4-methoxyphenyl) aldimine.

Aziridines have widely been recognized as being extremely versatile synthetic intermediates in organic synthesis.[1] Attributable to ring strain, the reaction of aziridines with a variety of nucleophiles leads to highly regio- and stereoselective ring-opening with carbon–carbon or carbon–heteroatom bond-formation. Aziridine rings are sometimes found in the substances which exhibit antitumor and antibiotic activities, for example, mitomycins and azinomycins.[2] It is now recognized that the aziridine ring is essential for such activities.[3] In all the reactions mentioned above, aziridines act as electrophiles **1**. In contrast to this, a very limited number of reactions in which aziridines act as nucleophiles has been reported. One such aziridine is a carbanion of aziridine, named aziridinyl anion **2** (Fig. 1).[4]

Aziridinyl anions are classified into two categories. One is the aziridinyl anions having a carbanion stabilizing group on the carbanionic carbon **3a** (stabilized aziridinyl anion).[5] The other is the aziridinyl anions having a hydrogen or a carbanion destabilizing group on the carbanionic carbon **3b** (nonstabilized aziridinyl anion).[6]

We previously reported the first generation of aziridinylmagnesium **5a** from sulfinylaziridines **4** by a sulfoxide–magnesium exchange reaction of sulfoxides[7] with ethylmagnesium bromide.[6d,e] In continuation of our studies on the generation of aziridinyl anions by the sulfoxide–metal exchange reaction, herein we report in detail a new method for the generation of aziridinyllithiums **5b** from **4** with *tert*-butyllithium.[8] The properties and reactivity of the generated aziridinyllithiums **5b** and some applications to the synthesis of α,α-dialkylamino acid derivatives **7**, including an optically active form, from **6** are also described (Scheme 1).

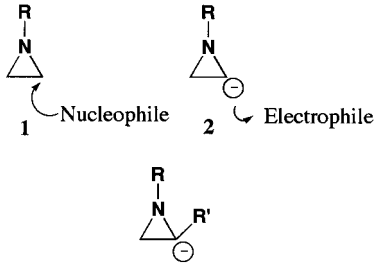

Figure 1.

Keywords: aziridinyllithiums; sulfinylaziridines; sulfoxide–lithium exchange; α,α-dialkylamino acid esters.
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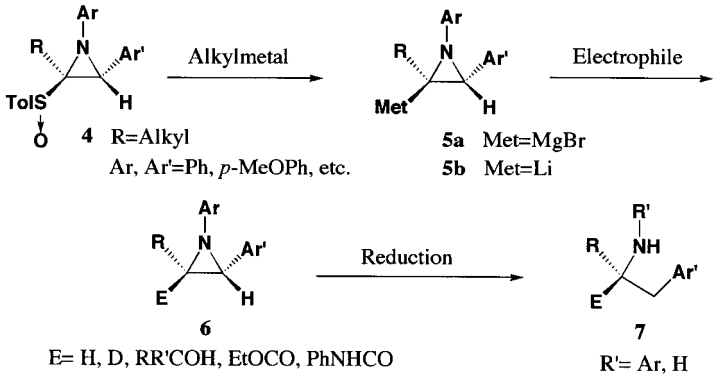


Scheme 1.

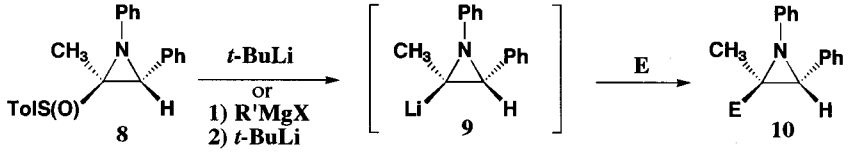
Results and Discussion

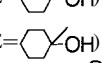
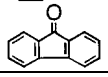
Generation of aziridinyllithiums from sulfinylaziridines with *tert*-butyllithium and studies on the properties and reactivity

We previously reported a method for generation of aziridinylmagnesiums **5a** from **4**.[6d,e] Also, we extensively studied generation of oxiranyl anions from sulfinyloxiranes.[9] Based on these studies we investigated if generation of aziridinyllithium **5b** was feasible by the sulfoxide–lithium exchange reaction of the sulfinylaziridine **4** with *t*-BuLi.

First, (*E*)-2-methyl-1,3-diphenyl-2-(*p*-tolylsulfinyl)aziridine **8** (see Table 1), which is easily synthesized from 1-chloroethyl *p*-tolyl sulfoxide and benzalaniline in two steps in high yield,[6e] in THF at −78°C was treated with *t*-BuLi (a solution of *t*-BuLi was added to a solution of **8** in THF). The reaction took place immediately. After 1 min, the reaction was quenched by adding deuterio methanol (CD_3OD) to give a quantitative yield of the desulfinylated product **10a** (see Table 1, entry 1). Though special precaution was taken to remove the proton source, the rate of deuterium incorporation was only less than 67%. To increase the deuterium incorporation we tried other experimental conditions

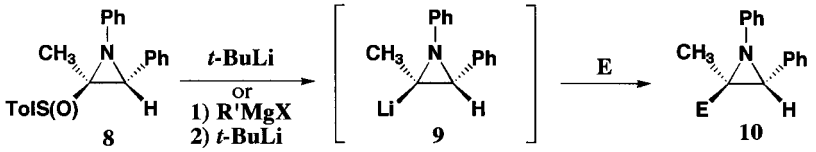
Table 1. Generation of 2-lithioaziridine **9** from *N*-phenylsulfinylaziridine **8** and reaction with deuterio methanol and carbonyl compound

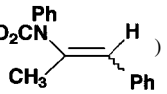


Entry	Alkylmetal (equiv.)	Temp. (°C)	Electrophile	Product/yield (%)[a]
1	*t*-BuLi (1.8)	−78	CD_3OD	**10a** 99 (E=D; 67%)[b]
2	*t*-BuLi (2)[c]	−78	CD_3OD	**10a** 55 (E=D; 65%)[b]
3	*t*-BuLi (3)[c]	−100	H_2O	**10b** 58 (E=H)
4	*t*-BuMgCl (1.5),*t*-BuLi (1.5)	−70	CD_3OD	**10a** 96 (E=D; 92%)[b]
5	MeMgBr (1), *t*-BuLi (1.5)	−70	CD_3OD	**10a** 94 (E=D; 90%)[b]
6	*t*-BuMgCl (1.5), *t*-BuLi (1.5)	−70∽−30	CD_3OD	**10a** 91 (E=D; 83%)[b]
7	MeMgBr (1), *t*-BuLi (1.5)	−70∽−30	CD_3OD	**10a** 96 (E=D; 86%)[b]
8	MeMgBr (1), *t*-BuLi (1.5)	−70∽r.t.	CD_3OD	**10b** 90 (E=H)
9	*t*-BuLi (1.8)	−78	CH_3CH_2CHO	**10c** (L)[d] 30 (E=CH(OH)Et) (P)[d] 40
10	*t*-BuMgCl (1.5), *t*-BuLi (1.5)	−70	PhCHO	**10d** (L)[d] 18 (E=CH(OH)Ph) (P)[d] 15
11	MeMgBr (1), *t*-BuLi (1.2)	−100	PhCHO	**10d** (L)[d] 37 (E=CH(OH)Ph) (P)[d] 33
12	MeMgBr (1), *t*-BuLi (1.8)	−78	CH_3COCH_3	**10e** 29 (E=C(OH)Me_2)
13	MeMgBr (1), *t*-BuLi (1.5)	−100	CH_3COCH_3	**10e** 41 (E=C(OH)Me_2)
14	MeMgBr (1), *t*-BuLi (1.5)	−70		**10f** 28 (E= )
15	MeMgBr (1), *t*-BuLi (1.5)	−100		**10f** 38 (E= )
16	MeMgBr (1), *t*-BuLi (2)	−68		**10g** 35 (E=)

[a] Isolated yield after silica gel column chromatography.
[b] The deuterium incorporation was measured from ^1H NMR.
[c] A solution of **8** in THF was added to a solution of *t*-BuLi (inverse addition).
[d] Less polar diastereomer (L) and more polar diastereomer (P) on silica gel TLC.

Table 2. Generation of 2-lithioaziridine **9** from *N*-phenylsulfinylaziridine **8** and reaction with electrophiles



Entry	Alkylmetal (equiv.)	Temp (°C)	Electrophile	Product/yield (%)[a]
1	MeMgBr (1), *t*-BuLi (1.5)	−70	$ClCO_2Et$	**10h** 47 (E=CO_2Et)
				10i 38 (E= )
2	MeMgBr (2), *t*-BuLi (2)	−100	$ClCO_2Et$	**10h** 75 (E=CO_2Et)
3	MeMgBr (2), *t*-BuLi (2)	−100	$ClCO_2Me$	**10j** 61 (E=CO_2Me)
4	MeMgBr (1), *t*-BuLi (1.5)	−70∽−30	$(EtO)_2POCl$	**10k** 43 (E=$PO(OEt)_2$)
5	MeMgBr (1), *t*-BuLi (2)	−78∽−30	CH_3I/DMPU[b]	0[c]
6	MeMgBr (1), *t*-BuLi (2)	−78∽−30	$C_6H_5CH_2Br$/DMPU[b]	0[c]

[a] Isolated yield after silica gel column chromatography.
[b] DMPU=*N*,*N*-dimethylpropyleneurea.
[c] This reaction gave the *N*-phenylaziridine **10b** (E=H) in 95 and 89% yields, respectively.

which were found to be effective in our oxiranyllithium case.[9] Thus, a THF solution of **8** was added to a THF solution of *t*-BuLi (entries 2 and 3, Table 1). However, in contrast to the oxiranyllithium case, this treatment markedly reduced the yield of **10a** and gave similar deuterium incorporation.

At this stage we considered that a trace of moisture in THF was the proton source of the above-mentioned reaction. In our previous study we found that the sulfinylaziridine **8** did not react at all with *t*-BuMgCl and MeMgBr.[6d,e] We tried to use these Grignard reagents for removing the moisture in THF. Thus, *t*-BuMgCl was first added to a solution of **8** in THF at −70°C and the reaction mixture was stirred for 10 min, then *t*-BuLi was added. After 1 min, the reaction was quenched with CD_3OD to afford **10a** in 96% yield with up to 92% deuterium content (entry 4). Entry 5 shows that MeMgBr works equally well. Both *t*-BuMgCl and MeMgBr were used in this study. From these experiments we were indeed able to generate the nonstabilized aziridinyllithium.

Next, we investigated the stability of the generated aziridinyllithium **9**. As shown in entries 6 and 7, the generated **9** was slowly warmed to −30°C and then quenched with CD_3OD. The chemical yield of **10a** was found to be similar compared with the results in entries 4 and 5; however, a slight decrease of the deuterium incorporation was observed. Next, the solution of **9** was slowly warmed to room temperature and then quenched with CD_3OD (entry 8). The reaction mixture was still very clean and the yield of the desulfinylated aziridine was 90%. Somewhat to our surprise, no deuterium incorporation was observed in the product. In this reaction it is noted that *tert*-butyl *p*-tolyl sulfoxide was obtained as a by-product of the sulfoxide–lithium exchange reaction. As no deuterium incorporation was found in this *tert*-butyl *p*-tolyl sulfoxide, it is certain that the generated aziridinyllithium **9** picks up the hydrogen on THF at above −30°C.

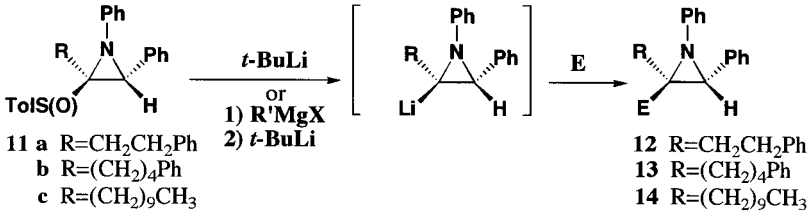
Reactivity of the generated aziridinyllithium **9** with several electrophiles was investigated and the results are summarized in Table 1 (entries 9–16). Propionaldehyde reacted with **9** in good yield without the Grignard reagent (entry 9). Benzaldehyde gave adducts; however, the yields were low (entry 10). In this case, lowering the reaction temperature to −100°C was found to be effective (entry 11). The reaction with ketones also gave adducts; however, the yields were less than 41%. In these cases, slightly better yields were obtained at −100°C (entries 12–15). In case of the reaction with 9-fluorenone, higher temperature was required to give the adduct **10g**.

Table 2 shows the results of the reaction of the aziridinyllithium **9** with other electrophiles. The reaction of **9** with ethyl chloroformate at −70°C gave the desired ester **10h** in 47% yield with ring-opened urethane derivative **10i** (entry 1). The formation of the urethane was prevented when this reaction was carried out at −100°C and the desired **10h** was obtained in 75% yield (entry 2). In the case with diethylchlorophosphate, the reaction did not proceed at −70°C (entry 4). Trials to obtain the alkylated aziridine were fruitless under several reaction conditions (entry 5 and 6).

We next investigated the generation of aziridinyllithiums from the sulfinylaziridines **11a**, **11b**, and **11c** (see Table 3). The sulfinylaziridine having 2-phenylethyl group **11a** gave the desulfinylated aziridine **12a** and **12b** in quantitative yield; however, the deuterium incorporation was found to be less than 83% (entry 3). Ethoxycarbonylation of the generated aziridinyllithium gave the ester **12c**. In this case, the establishment of the reaction conditions was found to be rather difficult (see entries 5 and 6).

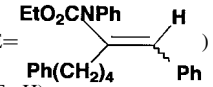
The sulfinylaziridine having 4-phenylbutyl group **11b** also gave aziridinyllithium in good yield (entries 7 and 8). The aziridinyllithium gave the adducts **13c** with propionaldehyde in moderate yields (entries 9 and 10). The aziridinyllithium gave the adduct with acetone in low yield (entries 11 and 12). The reaction of the aziridinyllithium with ethyl chloroformate was again found to be difficult

Table 3. Generation of 2-lithioaziridine from *N*-phenylsulfinylaziridine **11** and reaction with electrophiles



11 a R=CH_2CH_2Ph
b R=$(CH_2)_4Ph$
c R=$(CH_2)_9CH_3$

12 R=CH_2CH_2Ph
13 R=$(CH_2)_4Ph$
14 R=$(CH_2)_9CH_3$

Entry		Alkylmetal (equiv.)	Temp (°C)	Electrophile	Product/yield (%)[a]
1	**11a**	MeMgBr (2), *t*-BuLi (1.5)	−70	CD_3OD	**12a** 99 (E=D; 63)[b]
2	**11a**	*t*-BuMgCl (3), *t*-BuLi (1.5)	−70	CD_3OD	**12a** 99 (E=D; 73)[b]
3	**11a**	*t*-BuMgCl (3), *t*-BuLi (2)	−80	CD_3OD	**12a** 99 (E=D; 83)[b]
4	**11a**	*t*-BuMgCl (2.3), *t*-BuLi (2)	−70	CH_3OH	**12b** 94 (E=H)
5	**11a**	*t*-BuMgCl (2), *t*-BuLi (2)	−100	$ClCO_2Et$	**12c** 22 (E=CO_2Et)
6	**11a**	*t*-BuMgCl (2), *t*-BuLi (4)	−80	$ClCO_2Et$	**12c** 60 (E=CO_2Et)
7	**11b**	*t*-BuLi (1.5)	−70	H_2O	**13a** 86 (E=H)
8	**11b**	MeMgBr (1), *t*-BuLi (1.5)	−70	CD_3OD	**13b** 99 (E=D; 82)[b]
9	**11b**	MeMgBr (1), *t*-BuLi (1.5)	−78	CH_3CH_2CHO	**13c** (L) 21 (P) 27 (E=CH(OH)Et)
10	**11b**	MeMgBr (1), *t*-BuLi (1.5)	−100	CH_3CH_2CHO	**13c** (L) 34 (P) 28 (E=CH(OH)Et)
11	**11b**	MeMgBr (1), *t*-BuLi (1.5)	−70	CH_3COCH_3	**13d** 10 (E=$C(OH)Me_2$)
12	**11b**	MeMgBr (1), *t*-BuLi (1.5)	−100	CH_3COCH_3	**13d** 27 (E=$C(OH)Me_2$)
13	**11b**	MeMgBr (1), *t*-BuLi (1.5)	−70	$ClCO_2Et$	**13e** 28 (E=CO_2Et)
					13f 12 (E= )
14	**11c**	*t*-BuMgCl (3), *t*-BuLi (2)	−80	CH_3OH	**14a** 99 (E=H)
15	**11c**	*t*-BuMgCl (3), *t*-BuLi (2)	−80	CD_3OD	**14b** 99 (E=D; 72)[b]
16	**11c**	MeMgBr (3), *t*-BuLi (4)	−80	$ClCO_2Et$	**14c** 81 (E=CO_2Et)

[a] Isolated yield after silica gel column chromatography.
[b] The deuterium incorporation was measured from ^1H NMR.

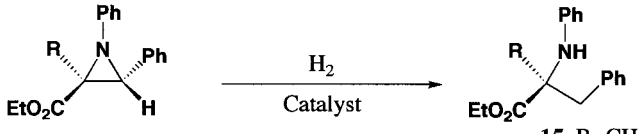
and the urethane derivative **13f** was obtained as a byproduct (entry 13).

The sulfinylaziridine having decyl group **11c** gave the desulfinylated aziridine in quantitative yield. In this case, the reaction of the generated aziridinyllithium with ethyl chloroformate gave the desired ester **14c** in relatively good yield (entry 16).

In summary of the results mentioned above, we concluded that the sulfinylaziridines **8** and **11** reacted with *t*-BuLi at low temperature, even at −100°C, to give nonstabilized aziridinyllithiums in high yields. The aziridinyllithiums are found to be stable at low temperature. The nucleophilicity of the generated aziridinyllithum to ketones and aldehydes was found to be relatively low. The reaction of the aziridinyllithiums with ethyl chloroformate gave moderate to good yields of the esters. But this reaction required some special conditions, for example, with regard to temperature of the reaction and the amount of *t*-BuLi, to get good yields.

Synthesis of racemic and optically active α,α-dialkylamino acid esters

In order to extend our new method to a synthesis of



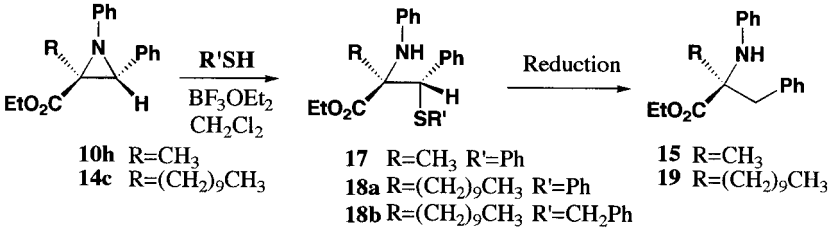
10h, 12c, 14c

15 R=CH_3
16 R=CH_2CH_2Ph

10h	R=CH_3	Raney-Ni / EtOH	2.5 h	**15** 50%
10h	R=CH_3	10% Pd-C / EtOH	2.3 h	**15** 64%
10h	R=CH_3	$Pd(OH)_2$ / EtOH	3 h	**15** 59%
12c	R=CH_2CH_2Ph	$Pd(OH)_2$ / MeOH	30 h	**16** 36%
12c	R=CH_2CH_2Ph	5% Rh-Al_2O_3 / MeOH	40 h	no reaction
14c	R=$(CH_2)_9CH_3$	$Pd(OH)_2$ / MeOH	100 h	complex mixture

Scheme 2. Catalytic hydrogenation of 2-carbethoxy aziridines **10h**, **12c**, and **14c**.

Table 4. Ring-opening of the aziridines **10h** and **14c** with thiols and reduction of the sulfides **17** and **18**



Entry		R′SH	Yield of sulfide		Reducing agent	Product	
1	**10h**	PhSH	**17**	74%	Raney-Ni/EtOH	**15**	42%
2	**14c**	PhSH	**18a**	92%	Raney-Ni/EtOH	**19**	34%
3	**14c**	$PhCH_2SH$	**18b**	87%	Raney-Ni/EtOH	**19**	53%
4			**18b**		Bu_3SnH/AIBN Benzene, reflux	**19**	62%

α,α-dialkylamino acid esters, we investigated regioselective ring-opening of the aziridinyl esters **10h**, **12c**, and **14c**. First, catalytic hydrogenation[10] of the aziridinyl esters was studied and the results are summarized in Scheme 2. The aziridinyl ester having a methyl group **10h** was smoothly hydrogenated with a Pd–C or $Pd(OH)_2$ catalyst in alcohol as a solvent under H_2 atmosphere. Even Raney-nickel in ethanol at room temperature was effective for the reduction.

In contrast to this result, hydrogenation of the aziridinyl ester having 2-phenylethyl group **12c** took place very slowly and the desired product **16** was obtained in only 36% yield. Hydrogenation of **12c** with Rh-Al_2O_3 did not proceed at all. The hydrogenation of **14c** showed a much worse result. The reaction did not proceed when even excess $Pd(OH)_2$ was used and prolonging the reaction gave a complex mixture, from which we could not obtain the desired product.

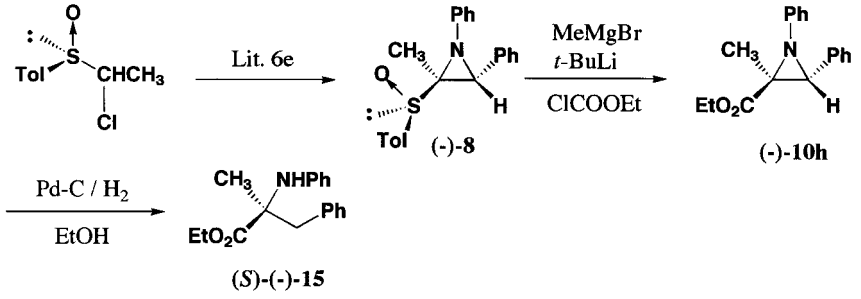
Next, we studied the regioselective ring-opening of the aziridinyl esters **10h** and **14c** with a thiol[11] and the reduction of the resultant sulfides (see Table 4). After some investigation we found that a thiol in the presence of BF_3OEt_2 in CH_2Cl_2 was the conditions of choice for the ring-opening. Under these conditions both aziridinyl esters **10h** and **14c** gave good yields of the sulfides **17** and **18a**, respectively (entries 1 and 2). Reductive desulfurization of the sulfides with Raney-nickel under the usual conditions, however, gave only moderate yields of the esters **15** and **19** (entries 1 and 2).

As we were eagerly seeking a method to get the α,α-dialkylamino ester **19**, we further investigated another thiol and the reduction conditions. The results are shown in entries 3 and 4. The ring-opening of **14c** with benzyl mercaptan gave a similar yield of the sulfide **18b** (compare entry 3 with entry 2). Reductive desulfurization of **18b** with Raney-nickel gave 53% yield of **19**. When this reduction was conducted with tributyltin hydride[12] in the presence of AIBN the yield of **19** was improved to 62% yield (entry 4).

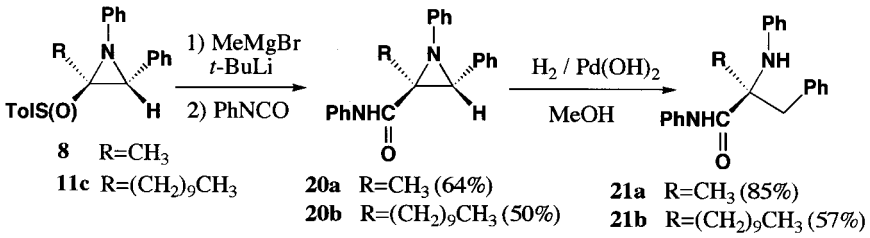
In order to extend the above-mentioned method to a synthesis of optically active α,α-dialkylamino acid esters, optically pure sulfinylaziridine (−)-**8** was synthesized from optically active 1-chloroethyl *p*-tolyl sulfoxide[6e] (Scheme 3). Optically active (−)-**8** was converted to ethylester (−)-**10h**, which was hydrogenated with Pd–C under hydrogen atmosphere, as described above, to give optically pure α,α-dialkylamino acid ester (*S*)-(−)-**15**. Optical purity was unambigously determined by HPLC using a chiral stationary column.[13]

Reaction of the aziridinyllithiums with phenyl isocyanate and a synthesis of α,α-dialkylamino acid amides

As described above, generation of the aziridinyllithiums and trapping them with several electrophiles were successful. Especially, reaction of aziridinyllithiums with ethyl chloroformate led to a new method for asymmetric synthesis of α,α-disubstituted amino acid esters. However, we found that the ethoxycarbonylation required rather delicate conditions and the reproducibility of the yield was sometimes low.



Scheme 3.



Scheme 4.

In order to overcome this problem, we investigated the reaction with other electrophiles and found that phenyl isocyanate was the reagent of choice. For example, reaction of the aziridinyllithium generated from **8** with excess phenyl isocyanate at −100°C for 10 min gave the desired aziridinyl amide **20a** in 64% yield (Scheme 4). This yield is not so high compared with the best yield of the ethoxycarbonylation (75%; see Table 2, entry 2); however, the yield for the amide **20a** was found to be reproducible. In a similar manner, **11c** gave **20b** in moderate yield.

Catalytic hydrogenation of the aziridine ring of **20a** and **20b** is quite interesting. Under similar conditions for the hydrogenation of ester **10h** (see Scheme 2), amide **20a** gave the ring-opened product in much higher yield (85%) within 1 h. In the case of ester **10h**, the yield was 59% and required 3 h for completion of the reaction. In the case of the hydrogenation of amide **20b**, the reaction required 5.5 h. The reaction gave a rather clean reaction mixture and the desired amide **21b** was obtained in 57% yield. Note that the corresponding ester **14c** gave only a complex mixture under similar conditions for 100 h (see Scheme 2).

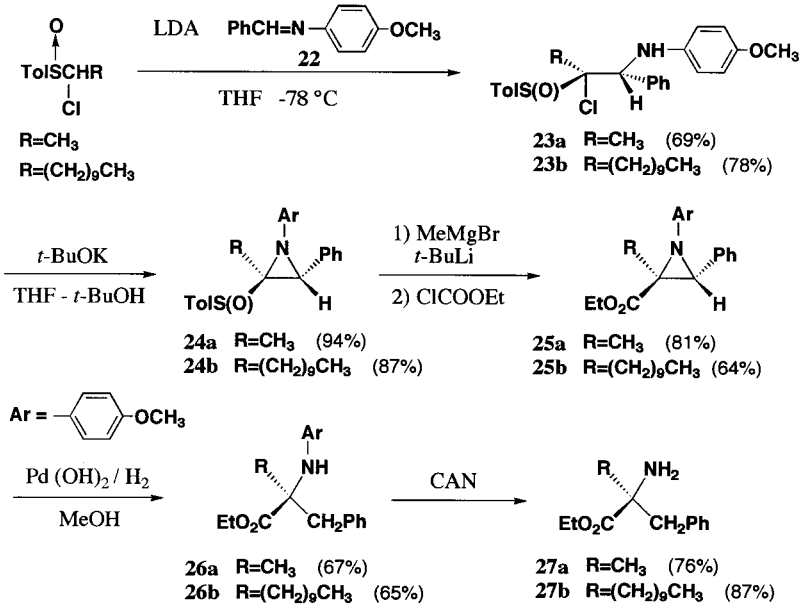
Synthesis of *N*-(4-methoxyphenyl) sulfinylaziridines and conversion of them to *N*-non substituted α,α-dialkylamino acid esters

Because all the sulfinylaziridines **4** were synthesized starting from 1-chloroalkyl *p*-tolyl sulfoxides and *N*-arylaldimines, the final products, α,α-dialkylamino acid esters and amides, have an aryl group on the nitrogen. In order to synthesize *N*-non substituted amino acid derivatives, we investigated the above-mentioned procedure by using *N*-(*p*-methoxyphenyl)aldimin **22** and obtained quite interesting results (Scheme 5).

Addition of the lithium α-sulfinyl carbanion of 1-chloroalkyl *p*-tolyl sulfoxides to the imine **22** at −78°C gave the adducts **23a** and **23b**, respectively, as crystals in good yields. These adducts are single diastereomers as described in the previous paper.[6e] Treatment of **23** with *t*-BuOK at 70°C gave the desired *N*-(4-methoxyphenyl) sulfinylaziridines **24a** and **24b** in high yields.

Generation of the aziridinyllithium of **23a** was carried out in a similar way as described above at −80°C and the generated aziridinyllithium was treated with ethyl chloroformate for 1 min. This reaction worked quite well to afford the ethoxycarbonylated aziridine **25a** in 81% yield. Moreover, this reaction was found to be reproducible and no ring-opened urethane derivative was obtained. In the case of the reaction with **24b**, again the ring-opened urethane was not observed and the ethoxycarbonylation was found to be reproducible to give **25b** in 64% yield.

Hydrogenolysis of the aziridine ring of **25a** and **25b** was also very interesting. The aziridine ring of both **25a** and **25b** was reduced by using $Pd(OH)_2$ as a catalyst in methanol at



Scheme 5.

room temperature within 3 h. Compared with the result in the same reaction of **14c** (Scheme 2), the 4-methoxyphenyl group is thought to activate the hydrogenolysis of the N–C bond. Removal of the 4-methoxyphenyl group of **26** was carried out with ceric (IV) ammonium nitrate (CAN)[14] smoothly to give *N*-non substituted α,α-dialkylamino acid ethyl esters **27a** and **27b** in good yields.

Experimental

All melting points are uncorrected and were measured with a Yanagimoto micro melting point apparatus. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometer. Electrom-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Optical rotations were taken with a JASCO DIP-1000 didital polarimeter. Silical gel 60 (MERCK) and silica gel 60N for flash chromatography (Kanto Chemical Co.) containing 0.5% fluorescence reagent 254 and quartz column were used for column chromatography and the flash column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry reagent and solvent, diisopropylamine was distilled from CaH_2 and THF was distilled from sodium diphenylketyl. All the reagents are commercially available and purified by recrystallization or distillation before use. Methanol and liquid N_2 were used for the cooling bath at −100°C.

Sulfinylaziridines.[15] The sulfinylaziridines **8** and **11c** were reported previously.[6e] The sulfinylaziridines **11a** and **11b** were synthesized from 1-chloro-3-phenylpropyl *p*-tolyl sulfoxide and 1-chloro-5-phenylpentyl *p*-tolyl sulfoxide and benzalaniline in a similar manner described previously[6e] in high overall yields. (*E*)-1,3-Diphenyl-2-(2-phenylethyl)-2-(*p*-tolylsulfinyl)aziridine (**11a**): colorless crystals; mp 159–161°C (AcOEt–hexane). IR (KBr) 1596, 1492, 1058 (SO) cm^{-1}; ^{1}H NMR δ 1.3–1.6 (2H, m), 2.41 (3H, s), 2.99 (2H, t, *J*=8.4 Hz), 4.70 (1H, s), 6.9–7.7 (19H, m). Anal. Calcd for $C_{29}H_{27}NOS$: C, 79.60; H, 6.22; N, 3.20; S, 7.33. Found: C, 79.26; H, 6.11; N, 3.10; S, 7.38. (*E*)-1,3-Diphenyl-2-(4-Phenylbutyl)-2-(*p*-tolylsulfinyl)aziridine (**11b**): colorless crystals; mp 103–105°C ($CHCl_3$-hexane). IR (KBr) 1597, 1493, 1057 (SO) cm^{-1}; ^{1}H NMR δ 1.0–1.2 (2H, m), 1.3–1.6 (2H, m), 1.7–1.9 (2H, m), 2.41 (3H, s), 2.54 (2H, m), 4.63 (1H, s), 7.0–7.6 (19H, m). MS *m*/*z* (%) 465 (M^+, 0.5), 449 (2), 339 (1), 326 (36), 236 (71), 182 (94), 91 (100). Calcd for $C_{31}H_{31}NOS$: M, 465.2126. Found: *m*/*z* 465.2139.

General procedure for a generation of aziridinyllithium 9. A synthesis of 2-deuterio-2-methyl-1.3-diphenylaziridine **10a** (Table 1, entry 5) is described. A solution of MeMgBr (0.18 mmol) in THF was added dropwise to a solution of **8** (62 mg; 0.18 mmol) in 4 ml of THF at −70°C under Ar atmosphere. The reaction mixture was stirred at −70°C for 10 min. *t*-BuLi (0.27 mmol) in pentane was added to the reaction mixture and after 2 min, the reaction was quenched by adding 0.2 ml of CD_3OD. The solution was stirred for 15 min, then sat. aq. NH_4Cl was added. The whole was extracted with ether–hexane and the product was purified by silica gel column chromatography to give 36 mg (94%) of **10a**[6e] as a colorless oil.

(*E*)-2-(1-Hydroxypropyl)-2-methyl-1,3-diphenylaziridine (10c). *t*-BuLi (0.41 mmol) was added to a solution of **8** (79 mg; 0.23 mmol) in 12 ml of THF with stirring at −78°C. After 1 min, propionaldehyde (0.69 mmol) was added and the reaction mixture was stirred at −78°C for 10 min. The reaction was quenched by adding sat. aq. NH_4Cl and the whole was extracted with ether–hexane. The products were purified by silica gel column chromatography to afford the adducts **10c**–**L** (18 mg; 30%) and **10c**–**P** (24.5 mg; 40%) together with **10b**[6e] (14.6 mg; 30%). **10c**–**L**: colorless viscous oil; IR (neat) 3585, 3447 (OH), 1596, 1488 cm^{-1}; ^{1}H NMR δ 0.97 (3H, t, *J*=7 Hz), 1.08 (3H, s), 1.63 (1H, m), 1.79 (1H, m), 3.75 (1H, s), 3.86 (1H, dd, *J*=7.9, 2.6 Hz), 6.9–7.5 (10H, m). MS *m*/*z* (%) 267 (M^+, 8), 220 (1), 208 (3), 182 (100). Calcd for $C_{18}H_{21}NO$: M, 267.1622. Found: *m*/*z* 267.1628. **10c**–**P**: colorless viscous oil; IR (neat) 3585, 3450 (OH), 1597, 1489 cm^{-1}; ^{1}H NMR δ 0.97 (3H, t, *J*=7.3 Hz), 1.15 (3H, s), 1.6–1.7 (2H, m), 3.07 (1H, m), 3.18 (1H, s), 6.9–7.5 (10H, m). MS *m*/*z* (%) 267 (M^+, 9), 250 (2), 208 (12), 176 (100). Calcd for $C_{18}H_{21}NO$: M, 267.1622. Found: *m*/*z* 267.1634.

(*E*)-2-[(Hydroxy)phenylmethyl]-2-methyl-1,3-diphenylaziridine (10d). 10d–**L**: colorless viscous oil; IR (neat) 3565, 3450 (OH), 1595, 2489 cm^{-1}; ^{1}H NMR δ 0.85 (3H, s), 1.18 (1H, d, *J*=3 Hz, OH), 4.23 (1H, s), 5.05 (1H, d, *J*=3 Hz), 6.9–7.5 (15H, m). MS *m*/*z* (%) 315 (M^+, 9), 296 (3), 224 (22), 182 (100). Calcd for $C_{22}H_{21}NO$: M, 315.1622. Found: *m*/*z* 315.1637. **10d**–**P**: colorless needles; mp 74–78°C (AcOEt–hexane); IR (KBr) 3580, 3290 (OH), 1595, 1489 cm^{-1}; ^{1}H NMR δ 1.11 (3H, s), 2.08 (1H, d, *J*=3 Hz, OH), 3.52 (1H, s), 4.33 (1H, d, *J*=3 Hz), 7.0–7.5 (15H, m). MS *m*/*z* (%) 315 (M^+, 12), 296 (4), 224 (19), 182 (100). Calcd for $C_{22}H_{21}NO$: M, 315.1622. Found: *m*/*z* 315.1627.

(*E*)-2-(1-Hydroxy-1-methylethyl)-2-methyl-1,3-diphenylaziridine (10e). Colorless needles; mp 86–88°C (AcOEt–hexane); IR (KBr) 3572 (OH), 1593, 1485 cm^{-1}; ^{1}H NMR δ 1.15, 1.30, 1.56 (each 3H, s), 3.95 (1H, s), 6.9–7.4 (10H, m). MS *m*/*z* (%) 267 (M^+, 10), 234 (3), 208 (6), 182 (100). Calcd for $C_{18}H_{21}NO$: M, 267.1622. Found: *m*/*z* 267.1624.

(*E*)-2-(1-Hydroxycyclohexyl)-2-methyl-1,3-diphenylaziridine (10f). Colorless viscous oil; IR (neat) 3572, 3470 (OH), 1597, 1491 cm^{-1}; ^{1}H NMR δ 1.14 (3H, s), 1.5–1.7 (8H, m), 1.8–2.0 (2H, m), 3.94 (1H, s), 6.8–7.0 (3H, m), 7.2–7.4 (7H, m). MS *m*/*z* (%) 307 (M^+, 10), 216 (18), 182 (100). Calcd for $C_{21}H_{25}NO$: M, 307.1934. Found: *m*/*z* 307.1925.

Aziridine (10g). Colorless needles; mp 162–164°C (AcOEt–hexane); IR (KBr) 3410 (OH), 1597, 1491 cm^{-1}; ^{1}H NMR δ 0.68 (3H, s), 3.94 (1H, s), 4.56 (1H, s, OH), 6.8–7.5 (18H, m). MS *m*/*z* (%) 389 (M^+, 11), 208 (100), 181 (94). Anal. Calcd for $C_{28}H_{23}NO$: C, 86.33; H, 5.96; N, 3.60. Found: C, 85.90; H, 5.93; N, 3.49.

(*E*)-2-Ethoxycarbonyl-2-methyl-1,3-diphenylaziridine (10h). Colorless oil; IR (neat) 1724 (CO), 1491, 1275, 1151 cm^{-1}; ^{1}H NMR δ 0.96 (3H, t, *J*=7 Hz), 1.33 (3H, s), 3.97 (2H, m), 4.15 (1H, s), 6.8–7.0 (3H, m), 7.3–7.5 (7H,

m). MS *m/z* (%) 281 (M^+, 15), 252 (21), 236 (28), 208 (43), 118 (100). Calcd for $C_{18}H_{19}NO_2$: M, 281.1415. Found: *m/z* 281.1425. (−)-10h: $[\alpha]_D^{25}=-94.25°$ (*c* 0.2, acetone).

Ethyl *N*-(1-methyl-2-phenylethyl)-*N*-phenylcarbamate (10i). Colorless oil; IR (neat) 1713 (CO), 1304, 1079 cm^{-1}; ^1H NMR δ 1.27 (3H, t, *J*=7 Hz), 2.12 (3H, s), 4.23 (2H, q, *J*=7 Hz), 6.48 (1H, s), 7.1–7.4 (10H, m). MS *m/z* (%) 281 (M^+, 100), 208 (70), 193 (52), 167 (50). Calcd for $C_{18}H_{19}NO_2$: M, 281.1415. Found: *m/z* 281.1429.

(*E*)-2-Methoxycarbonyl-2-methyl-1,3-diphenylaziridine (10j). Colorless oil; IR (neat) 1730 (CO), 1599, 1489, 1277, 1149 cm^{-1}; ^1H NMR δ 1.33 (3H, s), 3.53 (3H, s), 4.14 (1H, s), 6.8–7.0 (3H, m), 7.2–7.5 (7H, m). MS *m/z* (%) 267 (M^+, 35), 236 (83), 208 (100). Calcd for $C_{17}H_{17}NO_2$: M, 267.1258. Found: *m/z* 267.1265.

(*E*)-2-Diethylphosphonyl-2-methyl-1,3-diphenylaziridine (10k). Colorless oil; IR (neat) 1259, 1049, 1026 cm^{-1}; ^1H NMR δ 1.1–1.4 (6H, m), 1.50 (3H, s), 3.8–4.3 (5H, m), 6.9–7.5 (10H, m). MS *m/z* (%) 345 (M^+, 95), 316 (6), 288 (7), 207 (100). Calcd for $C_{19}H_{24}NO_3P$: M, 345.1492. Found: *m/z* 345.1483.

(*Z*)-2-Deuterio-1,3-diphenyl-2-(2-phenylethyl)aziridine (12a). Colorless oil; IR (neat) 1599, 1488, 1453, 697 cm^{-1}; ^1H NMR δ 1.63–1.78 (2H, m), 2.68–2.87 (2H, m), 3.33 (1H, s), 6.9–7.5 (15H, m). MS *m/z* (%) 300 (M^+, 20), 209 (100), 105 (93). Calcd for $C_{22}H_{20}DN$: M, 300.1736. Found: *m/z* 300.1737.

(*Z*)-2,3-Diphenyl-2-(2-phenylethyl)aziridine (12b). Colorless oil; IR (neat) 1599, 1488, 1454 cm^{-1}; ^1H NMR δ 1.64–1.75 (2H, m), 2.49 (1H, q, *J*=6.5 Hz), 2.68–2.87 (2H, m), 3.34 (1H, d, *J*=6.5 Hz), 6.9–7.5 (15H, m). MS *m/z* (%) 299 (M^+, 30), 208 (100), 104 (87). Calcd for $C_{22}H_{21}N$: M, 299.1673. Found: *m/z* 299.1676.

(*E*)-2-Ethoxycarbonyl-1,3-diphenyl-2-(2-phenylethyl)-aziridine (12c). Colorless oil; IR (neat) 1722 (CO), 1598, 1490, 1177 cm^{-1}; ^1H NMR δ 1.00 (3H, t, *J*=7 Hz), 1.84–2.06 (2H, m), 2.62–2.81 (2H, m), 4.01 (2H, q, *J*=7 Hz), 4.24 (1H, s), 6.9–7.5 (15H, m). MS *m/z* (%) 371 (M^+, 8), 281 (21), 280 (100), 208 (16). Calcd for $C_{25}H_{25}O_2N$: M, 371.1886. Found: *m/z* 371.1884.

(*Z*)-1,3-Diphenyl-2-(4-phenylbutyl)aziridine (13a). Colorless oil; IR (neat) 1601, 1489, 698 cm^{-1}; ^1H NMR δ 1.3–1.7 (6H, m), 2.41 (1H, q, *J*=6.6 Hz), 2.55 (2H, t, *J*=7 Hz), 3.30 (1H, d, *J*=6.6 Hz), 6.9–7.5 (15H, m). MS *m/z* (%) 327 (M^+, 100), 326 (49), 222 (49), 208 (37), 194 (29). Calcd for $C_{24}H_{25}N$: M, 327.1987. Found: *m/z* 327.1980.

(*Z*)-2-Deuterio-1,3-diphenyl-2-(4-phenylbutyl)aziridine (13b). Colorless oil; IR (neat) 1599, 1489, 694 cm^{-1}; ^1H NMR δ 1.3–1.7 (6H, m), 2.55 (2H, t, *J*=7 Hz), 3.29 (1H, s), 6.9–7.5 (15H, m). MS *m/z* (%) 328 (M^+, 100), 327 (49), 223 (41), 209 (33). Calcd for $C_{24}H_{24}DN$: M, 328.2045. Found: *m/z* 328.2057.

(*E*)-2-(1-Hydroxypropyl)-1,3-diphenyl-2-(4-phenylbutyl)-aziridine (13c). 13c–L: colorless oil; IR (neat) 3571 (OH), 1597, 1489, 698 cm^{-1}; ^1H NMR δ 0.54 (1H, d, *J*=4 Hz), 0.99 (3H, t, *J*=7 Hz), 1.0–1.2 (2H, m), 1.3–1.9 (6H, m), 2.58 (2H, t, *J*=7 Hz), 3.86 (1H, s), 4.09 (1H, m), 6.9–7.5 (15H, m). MS *m/z* (%) 385 (M^+, 5), 367 (3), 326 (12), 294 (77), 182 (76), 91 (100). Calcd for $C_{27}H_{31}NO$: M, 385.2406. Found: *m/z* 385.2403. **13c–P**: colorless viscous oil; IR (neat) 3570 (OH), 1597, 1489, 698 cm^{-1}; ^1H NMR δ 0.96 (3H, t, *J*=7 Hz), 1.0–1.2 (2H, m), 1.5–2.0 (7H, m), 2.53 (2H, t, *J*=8 Hz), 3.11 (1H, m), 3.20 (1H, s), 6.9–7.4 (15H, m). MS *m/z* (%) 385 (M^+, 6), 367 (3), 326 (8), 294 (100), 182 (66). Calcd for $C_{27}H_{31}NO$: M, 385.2406. Found: *m/z* 385.2399.

(*E*)-2-(1-Hydroxy-1-methylethyl)-1,3-diphenyl-2-(4-phenylbutyl)aziridine (13d). Colorless oil; IR (neat) 3570 (OH), 1597, 1494, 1488, 698 cm^{-1}; ^1H NMR δ 1.1–1.8 (6H, m), 1.33, 1.47 (each 3H, s), 2.54 (2H, t, *J*=7.5 Hz), 3.96 (1H, s), 6.9–7.4 (15H, m). MS *m/z* (%) 385 (M^+, 7), 352 (4), 326 (35), 182 (100). 167 (45). Calcd for $C_{27}H_{31}NO$: M, 385.2406. Found: *m/z* 385.2395.

(*E*)-2-Ethoxycarbonyl-1,3-diphenyl-2-(4-phenylbutyl)-aziridine (13e). Colorless oil; IR (neat) 1724 (CO), 1599, 1273, 1174 cm^{-1}; ^1H NMR δ 0.93 (3H, t, *J*=7 Hz), 1.4–1.7 (6H, m), 2.46 (2H, t, *J*=7 Hz), 3.95 (2H, q, *J*=7 Hz), 4.15 (1H, s), 6.8–7.5 (15H, m). MS *m/z* (%) 399 (M^+, 49), 370 (34), 354 (8), 326 (56), 280 (36), 236 (74), 91 (100). Calcd for $C_{27}H_{29}NO_2$: M, 399.2199. Found: *m/z* 399.2210.

Ethyl *N*-[2-phenyl-1-(4-phenylbutyl)ethenyl]-*N*-phenylcarbamate (13f). Colorless oil; IR (neat) 1718 (CO), 1597, 1302 cm^{-1}; ^1H NMR δ 1.25 (3H, t, *J*=7 Hz), 1.5–1.7 (4H, m), 2.36 (2H, t, *J*=7 Hz), 2.53 (2H, t, *J*=7 Hz), 4.21 (2H, q, *J*=7 Hz), 6.54 (1H, s), 7.1–7.4 (15H, m). MS *m/z* (%) 399 (M^+, 56), 370 (2), 326 (12), 308 (31), 281 (24), 91 (100). Calcd for $C_{27}H_{29}NO_2$: M, 399.2198. Found: *m/z* 399.2217.

(*Z*)-2-Decyl-2-deuterio-1,3-diphenylaziridine (14b). Colorless oil; IR (neat) 1599, 1488, 694 cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2–1.6 (18H, m), 3.30 (1H, s), 6.9–7.4 (10H, m). MS *m/z* (%) 336 (M^+, 78), 337 (19), 256 (16), 223 (86), 105 (100). Calcd for $C_{24}H_{32}NO$: M, 336.2675. Found: *m/z* 336.2677.

(*E*)-2-Octyl-2-ethoxycarbonyl-1,3-diphenylaziridine (14c). Colorless oil; IR (neat) 1726 (CO), 1598, 1490, 1272, 1174 cm^{-1}; ^1H NMR δ 0.86, 0.95 (each 3H, t, *J*=7 Hz), 1.1–1.7 (18H, m), 3.95 (2H, q, *J*=7 Hz), 4.12 (1H, s), 6.9–7.5 (10H, m). MS *m/z* (%) 407 (M^+, 34), 378 (45), 334 (82), 280 (41), 244 (100). Calcd for $C_{27}H_{37}NO_2$: M, 407.2824. Found: *m/z* 407.2824.

Ethyl 2-methyl-3-phenyl-2-phenylaminopropionate (15). A mixture of **10h** (79.5 mg) and 10% Pd–C (300 mg) in 2 ml of ethanol was stirred under H_2 atmosphere at room temperature for 2.3 h. The Pd–C was filtered off and the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography to afford 45 mg (64%) of **15** as colorless prisms; mp 79–82°C (AcOEt–hexane). IR (KBr) 3408 (NH), 1728 (CO), 1603, 1508 cm^{-1}; ^1H NMR δ 1.19 (3H, t, *J*=7 Hz), 3.21 (1H, d, *J*=14 Hz), 3.31 (1H, d, *J*=14 Hz), 4.18 (2H, q, *J*=7 Hz),

6.6–7.3 (10H, m). MS *m/z* (%) 283 (M^+,4), 210 (33), 192 (100), 182 (11), 118 (48). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.41; N, 4.96. Found: C, 76.21; H, 7.34; N, 4.79. (*S*)-(−)-**15**: Mp 93–94°C (AcOEt–hexane); $[\alpha]_D^{25}=-34.15°$ (*c* 0.2 acetone).

Ethyl 2-benzyl-4-phenyl-2-phenylaminobutanoate (16). Colorless oil; IR (neat) 3402 (NH), 1731 (CO), 1602, 1496, 1198 cm^{-1}; ^1H NMR δ 1.28 (3H, t, *J*=7 Hz), 2.3–2.7 (4H, m), 3.18, 3.51 (each 1H, d, *J*=14 Hz), 4.0–4.3 (3H, m), 6.7–7.7 (15H, m). MS *m/z* (%) 373 (M^+, 1), 282 (50), 230 (19), 178 (75), 91 (100). Calcd for $C_{25}H_{27}NO_2$: M, 373.2041. Found: *m/z* 373.2059.

Ethyl 2-methyl-3-phenyl-2-phenylamino-3-phenylthiopropionate (17). In a 30-ml dried flask was added thiophenol (0.04 ml) followed by BF_3-etherate (0.023 ml) at 0°C under Ar. A solution of **10h** (50 mg; 0.18 mmol) in 4 ml of CH_2Cl_2 was added dropwise to the mixture. The resulting reaction mixture was stirred at 0°C for 10 min, then at room temperature for 30 min. The reaction was quenched by adding aq. K_2CO_3 and the whole was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to give 60 mg (85%) of **17** as a colorless oil. IR (neat) 3401 (NH), 1731 (CO), 1601, 1504, 1236 cm^{-1}; ^1H NMR δ 1.17 (3H, t, *J*=7 Hz), 1.62 (3H, s), 4.13 (2H, q, *J*=7 Hz), 4.43 (1H, bs), 4.53 (1H, s), 6.7–7.5 (15H, m). MS *m/z* (%) 391 (M^+, 0.2), 318 (2), 299 (1), 192 (100). Calcd for $C_{24}H_{25}NO_2S$: M, 391.1606. Found: *m/z* 391.1610.

Ethyl 2-[(phenyl)phenylthiomethyl]-2-phenylaminododecanoate (18a). Colorless oil; IR (neat) 3401, 3368 (NH), 1732 (CO), 1601, 1496, 1259, 1211 cm^{-1}; ^1H NMR δ 0.86 (3H, t, *J*=7 Hz), 1.1–1.4 (19H, m), 1.94 (1H, m), 2.20 (1H, m), 4.21 (2H, m), 4.58 (1H, s), 5.10 (1H, s), 6.8–7.5 (15H, m). MS *m/z* (%) 517 (M^+, 0.1), 407 ([M-C_6H_5SH]$^+$, 29), 378 (37), 334 (92), 318 (84), 224 (100).

Ethyl 2-[(benzylthio)phenylmethyl]-2-phenylaminododecanoate (18b). Colorless oil; IR (neat) 3376 (NH), 1731 (CO), 1601, 1494, 1259, 1210 cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.0–1.4 (19H, m), 1.78 (1H, m), 2.05 (1H, m), 3.26, 3.50 (each 1H, d, *J*=13.3 Hz), 4.09 (1H, s), 4.15 (2H, m), 4.92 (1H, bs), 6.7–7.3 (15H, m). MS *m/z* (%) 531 (M^+, 0.1), 458 (1), 366 (1), 318 (100). Calcd for $C_{34}H_{45}NO_2S$: M, 531.3171. Found: *m/z* 531.3163.

Ethyl 2-benzyl-2-phenylaminododecanoate (19). Raney nickel (W2, about 230 mg) was added to a solution of **18b** (58 mg; 0.11 mmol) in 2 ml of EtOH and the suspension was stirred at room temperature for 30 min. The nickel was filtered off and the EtOH was evaporated. The product was purified by silica gel column chromatography to afford 23.5 mg (53%) of **19** as a colorless oil. IR (neat) 3406 (NH), 1731 (CO), 1603, 1511, 1196 cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.1–1.4 (19H, m), 1.90 (1H, m), 2.10 (1H, m), 3.23, 3.40 (each 1H, d, *J*=13.8 Hz), 4.18 (2H, m), 4.43 (1H, bs), 6.7–7.3 (10H, m). MS *m/z* (%) 409 (M^+, 1), 336 (16), 318 (100), 244 (18). Calcd for $C_{27}H_{39}NO_2$: M, 409.2978. Found: *m/z* 409.2969.

Reductive desulfurization of 18b with Bu_3SnH. Bu_3SnH (0.14 ml; 0.51 mmol) and AIBN (13 mg; 0.08 mmol) were added to a solution of **18b** (90.3 mg; 0.17 mmol) in 3 ml of benzene. The solution was stirred at room temperature for 10 min, then refluxed for 2 h under Ar atmosphere. The solvent was evaporated under vacuum and the product was purified by silica gel column chromatography to give **19** (62%).

Synthesis of amide 20a. MeMgBr (0.36 mmol) was added with stirring to a solution of **8** (62 mg; 0.18 mmol) in 2 ml of THF at −50°C under Ar atmosphere. The reaction mixture was stirred at −50°C for 10 min, then was cooled to −100°C. *t*-BuLi (0.36 mmol) was added to the reaction mixture and after 1 min phenyl isocyanate (0.75 mmol) was added. The reaction mixture was stirred at −100°C for 10 min, then the reaction was quenched by adding sat. aq. NH_4Cl. The whole was extracted with $CHCl_3$. The product was purified by flash column chromatography to give 38 mg (64%) of **20a** as colorless crystals; mp 153–155°C (AcOEt-hexane). IR (KBr) 3312 (NH), 1654 (CO), 1596, 1522, 1440 cm^{-1}; ^1H NMR δ 1.49 (3H, s), 4.15 (1H, s), 6.9–7.4 (15H, m). MS *m/z* (%) 328 (M^+,43), 236 (35), 208 (31), 182 (100). Anal. Calcd for $C_{22}H_{20}N_2O$: C, 79.46; H, 6.14; N, 8.53. Found: C, 79.73; H, 6.04; N, 8.31.

Amide 20b. Colorless crystals; mp 95–98°C (AcOEt–hexane). IR (KBr) 3364 (NH), 1663 (CO), 1598, 1531, 1441, 748, 697 cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.1–1.4 (13H, m), 1.4–1.7 (4H, m), 1.88 (1H, t, *J*=9 Hz), 4.10 (1H, s), 7.0–7.5 (15H, m). MS *m/z* (%) 454 (M^+, 70), 362 (18), 244 (55), 182 (100). Anal. Calcd for $C_{31}H_{38}N_2O$: C, 81.90; H, 8.42; N, 6.16. Found: C, 81.76; H, 8.54; N, 6.02.

Catalytic hydrogenation of 20a and 20b. To a solution of **20a** (33 mg) in 1 ml of distilled methanol was added $Pd(OH)_2$ on carbon (10 mg) and the suspension was stirred under H_2 atmosphere at room temperature for 1 h. The catalyst was filtered off and the product was purified by silica gel column chromatography to give **21a** (26 mg; 85%) as colorless crystals; mp 112–115°C (AcOEt–hexane). IR (KBr) 3297 (NH), 1667 (CO), 1602, 1532, 1495, 1439 cm^{-1}; ^1H NMR δ 1.46 (3H, s), 3.23, 3.44 (each 1H, d, *J*=14 Hz), 3.90 (1H, s), 6.6–7.5 (15H, m), 8.77 (1H, s). MS *m/z* (%) 330 (M^+, 3), 239 (44), 210 (100). Calcd for $C_{22}H_{22}N_2O$: M, 330.1732. Found: *m/z* 330.1722. **21b**: Colorless crystals; mp 64–65°C (hexane). IR (KBr) 3342 (NH), 1668 (CO), 1602, 1515, 1497, 1441 cm^{-1}; ^1H NMR δ 0.87 (3H, t, *J*=7 Hz), 1.1–1.9 (18H, m), 3.30, 3.49 (each 1H, d, *J*=14 Hz), 3.81 (1H, s), 6.6–7.5 (15H, m), 8.63 (1H, s). MS *m/z* (%) 456 (M^+, 2), 336 (100), 244 (23). Calcd for $C_{31}H_{40}N_2O$: M, 456.3140. Found: *m/z* 456.3150.

(1R*, 2R*)-2-Chloro-1-(4-methoxyphenylamino)-1-phenyl-2-(p-tolylsulfinyl)propane (23a). To a solution of LDA (2.4 mmol) in 7 ml of THF at −78°C was added a solution of 1-chloroethyl *p*-tolyl sulfoxide (405 mg; 2 mmol) in 2 ml of THF dropwise with stirring. After 10 min, a solution of the imine **22** (508 mg; 2.4 mmol) in THF was added to the reaction mixture and the reaction mixture was stirred at −78°C for 30 min. The reaction was quenched by sat. aq. NH_4Cl and the whole was extracted with $CHCl_3$. The organic layer was washed once with sat. aq. NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to give

colorless crystals, which was filtered and washed with a mixture of AcOEt–hexane (10:1) to give pure **23a** (570 mg; 69%); colorless crystals; mp 165–168°C (AcOEt–hexane). IR (KBr) 3302 (NH), 1509, 1252, 1037 (SO) cm^{-1}; ^1H NMR δ 1.84 (3H, s), 2.39 (3H, s), 3.68 (3H, s), 4.36 (1H, d, J=3 Hz), 5.75 (1H, d, J=3 Hz, NH), 6.39, 6.63 (each 2H, d, J=9 Hz), 7.2–7.6 (9H, m). MS m/z (%) 413 (M^+, 9), 361 (4), 273 (74), 238 (78), 212 (84), 122 (100). Anal. Calcd for $C_{23}H_{24}ClNO_2S$: C, 66.74; H, 5.84; Cl, 8.56; N, 3.38; S, 7.75. Found: C, 66.49; H, 5.72; Cl, 8.72; N, 3.18; S, 7.80.

(1R*, 2R*)-2-Chloro-1-(4-methoxyphenylamino)-1-phenyl-2-(p-tolylsulfinyl)dodecane (23b). Colorless crystals; mp 127–130°C (AcOEt-hexane). IR (KBr) 3293 (NH), 1514, 1251, 1039 (SO) cm^{-1}; ^1H NMR δ 0.88 (3H, t, J= 6.4 Hz), 1.2–2.0 (18H, m), 2.36 (3H, s), 3.68 (3H, s), 4.06 (1H, s), 6.23, 6.60 (each 2H, d, J=9 Hz), 7.1–7.7 (9H, m). MS m/z (%) 539 (M^+, 0.6), 399 (100), 272 (82). Anal. Calcd for $C_{32}H_{42}ClNO_2S$: C, 71.15; H, 7.84; Cl, 6.56, N, 2.59; S, 5.94. Found: C, 71.36; H, 7.82; Cl, 6.67; N, 2.41; S, 5.99.

(*E*)-2-Methyl-1-(4-methoxyphenyl)-3-phenyl-2-(*p*-tolylsulfinyl)aziridine (24a). To a solution of **23a** (621 mg; 1.5 mmol) in a mixture of THF (25 ml) and *t*-BuOH (25 ml) at 70°C was added a suspension of *t*-BuOK (450 mg; 4 mmol) in 5 ml of *t*-BuOH. The reaction mixture was stirred at 70°C for 40 min. After cooling the reaction mixture to room temperature, the reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with a mixture of benzene–ether. The product was purified by silica gel column chromatography to give **24a** (532 mg; 94%) as colorless crystals; mp 88–91°C (AcOEt–hexane). IR (KBr) 1505, 1238, 1228, 1046 (SO) cm^{-1}; ^1H NMR δ 1.03 (3H, s), 2.41 (3H, s), 3.78 (3H, s), 4.51 (1H, s), 6.86, 6.98 (each 2H, d, J=9 Hz), 7.2–7.7 (9H, m). MS m/z (%) 377 (M^+, 7), 361 (25), 238 (52), 212 (63), 148 (100). Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71; S, 8.49. Found: C, 73.31; H, 6.01; N, 3.52; S, 8.51.

(*E*)-2-Decyl-1-(4-methoxyphenyl)-3-phenyl-2-(*p*-tolylsulfinyl)aziridine (24b). Colorless oil; IR (neat) 1505, 1241, 1084, 1057 (SO) cm^{-1}; ^1H NMR δ 0.88 (3H, t, J=7 Hz), 1.0–1.3 (16H, m), 1.6–1.8 (2H, m), 2.41 (3H, s), 3.78 (3H, s), 4.62 (1H, s), 6.87, 7.05 (each 2H, d, J=9 Hz), 7.2–7.7 (9H, m). MS m/z (%) 503 (M^+, trace), 478 (1.4), 364 (28), 274 (100). Calcd for $C_{32}H_{41}NO_2S$: M, 503.2858. Found: m/z 503.2869.

(*E*)-2-Ethoxycarbonyl-1-(4-methoxyphenyl)-2-methyl-3-phenylaziridine (25a). To a solution of **24a** (280 mg; 0.74 mmol) in 25 ml of dry THF in a flame-dried flask was added MeMgBr (0.96 mmol) at −50°C with stirring. The reaction mixture was stirred at −50°C for 15 min, then the solution was cooled to −80°C. *t*-BuLi (1.48 mmol) was added to the reaction mixture dropwise with stirring and after 1 min, ethyl chloroformate 0.27 ml (2.8 mmol) was added. The reaction mixture was stirred for 1 min, then the reaction was quenched by adding sat. aq. NH_4Cl. The whole was extracted with ether–benzene. The product was purified by silica gel flash chromatography to afford **25a** (187 mg; 81%) as a colorless oil. IR (neat) 1723 (CO), 1506, 1274, 1241, 1150 cm^{-1}; ^1H NMR δ 1.02 (3H, t, J=7 Hz), 1.31 (3H, s), 3.76 (3H, s), 3.83–4.10 (2H, m), 4.20 (1H, s), 6.75–6.85 (4H, m), 7.33–7.43 (5H, m). MS m/z (%) 311 (M^+, 21), 282 (14), 238 (39), 189 (37), 148 (100). Calcd for $C_{19}H_{21}NO_3$: M, 311.1520. Found: m/z 311.1515.

(*E*)-2-Decyl-2-ethoxycarbonyl-1-(4-methoxyphenyl)-3-phenylaziridine (25b). Colorless oil; IR (neat) 1724 (CO), 1507, 1241, 1177 cm^{-1}; ^1H NMR δ 0.88 (3H, t, J=7 Hz), 1.02 (3H, t, J=7 Hz), 1.12–1.48 (18H, m), 3.76 (3H, s), 3.93–4.02 (2H, m), 4.13 (1H, s), 6.75–6.85 (4H, m), 7.28–7.44 (5H, m). MS m/z (%) 437 (M^+, 52), 408 (31), 364 (45), 276 (100), 274 (58). Calcd for $C_{28}H_{39}NO_3$: M, 437.2929. Found: m/z 437.2924.

Ethyl 2-benzyl-2-(4-methoxyphenyl)aminopropionate (26a). To a solution of **25a** (185 mg; 0.59 mmol) in distilled methanol (10 ml) was added 45 mg of $Pd(OH)_2$ (10% on carbon). The reaction mixture was stirred under H_2 atmosphere for 1 h. The catalyst was filtered off and the methanol was evaporated to give a residue, which was purified by silica gel column chromatography to give 125 mg (67%) of **26a** as a colorless oil. IR (neat) 3400 (NH), 1729 (CO), 1513, 1239 cm^{-1}; ^1H NMR δ 1.19 (3H, t, J=7 Hz), 1.42 (3H, s), 3.15, 3.24 (each 1H, d, J=13 Hz), 3.75 (3H, s), 4.16 (2H, q, J=7 Hz), 6.65, 6.76 (each 2H, d, J=8.8 Hz), 7.10–7.32 (5H, m). MS m/z (%) 313 (M^+, 10), 240 (32), 222 (100), 148 (67), 91 (13). Calcd for $C_{19}H_{23}NO_3$: M, 313.1676. Found: m/z 313.1672.

Ethyl 2-benzyl-2-(4-methoxyphenyl)aminododecanoate (26b). Colorless oil; IR (neat) 3407 (NH), 1731 (CO), 1513, 1239, 1195, 1040 cm^{-1}; ^1H NMR δ 0.88 (3H, t, J=7 Hz), 1.10–1.46 (21H, m), 3.21, 3.32 (each 1H, d, J=13 Hz), 3.77 (3H, s), 4.10–4.23 (2H, m), 6.63–6.79 (4H, m), 6.99–7.26 (5H, m). MS m/z (%) 439 (M^+, 7), 348 (100), 274 (17). Calcd for $C_{28}H_{41}NO_3$: M, 439.3087. Found: m/z 439.3090.

Ethyl 2-amino-2-benzylpropionate (27a). A solution of CAN (804 mg; 1.47 mmol) in 7 ml of water was added to a solution of **26a** (92 mg; 0.29 mmol) in 9 ml of CH_3CN at 0°C with stirring. The reaction mixture was stirred at 0°C for 30 min, then the solution was neutralized with 5% aq. $NaHCO_3$. Na_2SO_3 (110 mg) was added to the reaction mixture with stirring and after 10 min, the whole was extracted with ethyl acetate. The product was purified by silica gel column chromatography to afford 46.2 mg (76%) of **27a** as a colorless oil. IR (neat) 3376, 3310 (NH), 1730 (CO), 1194, 1104 cm^{-1}; ^1H NMR δ 1.26 (3H, t, J=7 Hz), 1.39 (3H, s), 2.80, 3.13 (each 1H, d, J=13 Hz), 4.10–4.20 (2H, m), 7.10–7.40 (5H, m). MS (FAB) m/z (%) 208 ($[M+H]^+$, 100), 134 (52), 116 (21), 91 (17). Calcd for $C_{12}H_{18}NO_2$: M, 208.1338. Found: m/z 208.1341.

Ethyl 2-amino-2-benzyldodecanoate (27b). Colorless oil; IR (neat) 3388 (NH), 1732 (CO), 1182, 1031 cm^{-1}; ^1H NMR δ 0.88 (3H, t, J=7 Hz), 1.10–1.70 (22H, m), 1.85–1.95 (1H, m), 2.76, 3.18 (each 1H, d, J=13 Hz), 4.09–4.23 (2H, m), 7.10–7.40 (5H, m). MS (FAB) m/z (%) 334 ($[M+H]^+$, 100), 260 (51), 242 (21), 91 (15). Calcd for $C_{21}H_{36}NO_2$: M, 334.2746. Found: m/z 334.2734.

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15. As reported in the lit. 6e, the sulfinylaziridines were synthesized starting from 1-chloroalkyl *p*-tolyl sulfoxides and imines. The lithium carbanions of the 1-chloroalkyl *p*-tolyl sulfoxides react with *N*-aryl aldimines, derived from arylamines and aryl aldehydes, in high yields; however, they do not react with *N*-alkyl aldimines, derived from alkylamines and aryl aldehydes or alkyl aldehydes. The synthesis of various kinds of the sulfinylaziridines other than those reported in this paper requires another synthetic method, which is now investigated in these laboratories.