Selected Paper

Highly Stereoselective Samarium(II) Iodide-Mediated Aldol Reactions of Acylaziridines with Aldehydes

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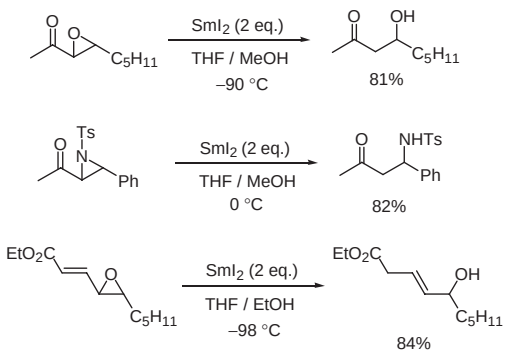
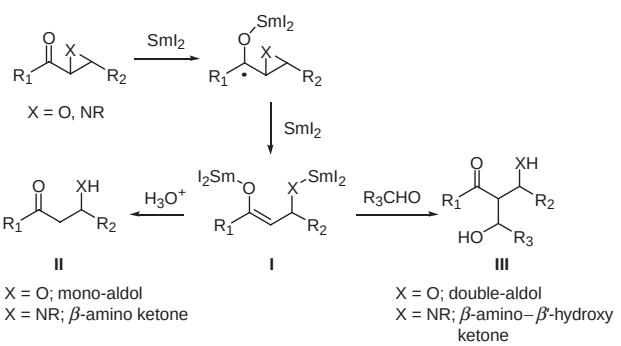
The samarium(II) iodide-mediated stereoselective aldol reactions of acylaziridines with aldehydes are described. β-Amino–β'-hydroxy ketones were synthesized in high yields by the aldol reaction of aldehydes with samarium enolates generated by aziridine-fragmentation of aziridinyl ketones with two moles of samarium(II) iodide. By the choice of an appropriate nitrogen protecting group, depending on the substituent at C-3 position of aziridinyl ketone, *anti*,*anti*-β-amino–β'-hydroxy ketones were diastereoselectively obtained among the four possible diastereomers. Further, enantiomerically pure *anti*,*anti*-β-amino–β'-hydroxy ketones were successfully obtained by this aldol reaction when chiral aziridinyl ketones were used. In addition, δ-amino–β'-hydroxy–β,γ-unsaturated esters were also synthesized in high yields by the aldol reaction of aldehydes with samarium enolates generated by aziridine-fragmentation and olefin-migration of γ,δ-aziridinyl–α,β-unsaturated esters using two moles of samarium(II) iodide. This aldol reaction proceeded with complete α-regioselectivity and formed (*E*)-olefin selectively. By introducing chiral oxazolidin-2-one auxiliary to γ,δ-aziridinyl–α,β-unsaturated carbonyl system, this reaction was extended successfully to the asymmetric reaction and enantiomerically pure *syn*-δ-amino–β'-hydroxy-β,γ-unsaturated esters were obtained in high yields.

Samarium(II) iodide (SmI_2) is known as a powerful one-electron reducing agent and a wide variety of functional groups can be reduced under mild conditions.[1] One of the most widely employed processes using SmI_2 is the reductive cleavage of α-hetero-substituted carbonyl compounds.[2] The reduction of substrates possessing small rings adjacent to the carbonyl group is known as a useful synthetic method. Oxiranyl ketones[3] and esters,[4] aziridinyl ketones and esters,[5] and vinyl oxiranes,[6] etc. are successfully reduced with SmI_2 in the presence of a proton source such as methanol and the corresponding ring-opening products are obtained (Scheme 1). It is known that these reactions proceed through successive one-electron transfer processes to generate samarium enolates **I**, followed by protonation at α-carbon atom (Scheme 2, **I** → **II**). These intermediates, samarium enolates **I**, are considered as nucleophilic enolates, which react with electrophiles such as aldehydes (**I** → **III**). This consideration prompted us to study SmI_2-mediated aldol reaction of oxiranyl ketones with aldehydes; expectedly, the reaction afforded 3-hydroxy-2-(1-hydroxyalkyl)alkyl ketones (double-aldols) in high yields.[7] This practical reaction was successfully applied to synthesis of taxane skeleton.[8] Then, the use of aziridinyl ketones instead of the above mentioned oxiranyl ketones was planned next in order to find its new possibility in synthetic chemistry. Thus formed aldol adducts are considered to be 3-amino-2-(1-hydroxyalkyl)alkyl ketones (β-amino–β'-hydroxy ketones).

In recent years, synthesis of β-amino acids has attracted considerable attention.[9] Among various substituted β-amino acids, especially β'-hydroxy derivatives are actually constituted as an important class of molecules with interesting chemical and biological properties, due to their similarity to serine and other unusual amino acids. Therefore, β-amino–β'-hydroxy ketones are considered as important analogues of β-amino–β'-hydroxy acids and are expected to work as useful building blocks for the synthesis of biologically important compounds;



Scheme 1.



Scheme 2.

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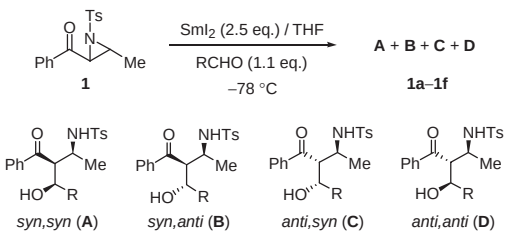
however, their syntheses have not yet been reported. In this paper, we would like to describe a new and efficient method for stereoselective synthesis of β-amino–β'-hydroxy ketones by the SmI_2-mediated aldol reaction of aziridinyl ketones with aldehydes.[10] A possible reaction mechanism is put forward that accounts for configurations of the resulting aldol adducts.

Results and Discussion

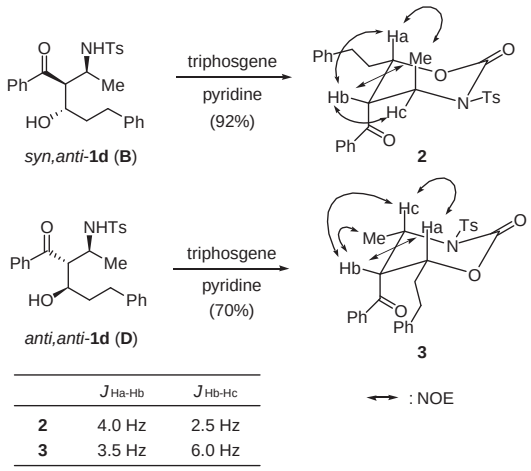
Stereoselective Synthesis of β-Amino–β'-Hydroxy Ketones by the Samarium(II) Iodide-Mediated Aldol Reaction of Aziridinyl Ketones with Aldehydes.[10] Aziridinyl ketones were prepared from the corresponding α,β-unsaturated ketones according to the literature procedures.[11,12] In the first place, the SmI_2-mediated aldol reaction of *trans*-2-benzoyl-3-methyl-1-tosylaziridine (**1**), an aryl aziridinyl ketone, with several aldehydes was examined (Table 1). The reaction of **1** with benzaldehyde was carried out at -78 °C in THF by adding a THF solution of SmI_2. The corresponding β-amino–β'-hydroxy ketone (**1a**) was obtained in a good yield (67/33 mixture of *syn*,*anti* (**B**) and *anti*,*anti* (**D**) isomers) along with a small amount of reduction product, β-*N*-tosylamino ketone (Entry 1). The yields of the products were greatly influenced by the substituents on the aromatic ring of the aldehydes (Entries 2 and 3). When 4-chlorobenzaldehyde having an electron-withdrawing substituent on the aromatic ring was used, no product was obtained because it was easily reduced by SmI_2 to promote competitive pinacol coupling. On the other hand, the reaction of **1** with aliphatic aldehydes proceeded smoothly to give the corresponding β-amino–β'-hydroxy ketones (**1c**–**1f**) in excellent yields (Entries 4–7). The reaction proceeded rapidly under nearly neutral conditions, and this is considered as one of the important factors which contribute to the high yielding of the products. All entries afforded the *syn*,*anti* (**B**) and *anti*,*anti* (**D**) isomers as major products among the four possible diastereomers. These results are similar to those of SmI_2-mediated formations of double-aldols by the reaction of oxiranyl ketones with aldehydes.[7]

Table 1. The SmI_2-Mediated Aldol Reaction of Aziridinyl Ketone (**1**) with Various Aldehydes



Entry	Aldehyde R	Product	Yield/%[a]	(**A**/**B**/**C**/**D**)[b]
1	Ph	**1a**	80	(0/67/0/33)
2	4-$MeOC_6H_4$	**1b**	85	(0/<5/0/>95)
3	4-ClC_6H_4		ND[c]	
4	Et	**1c**	95	(0/34/0/66)
5	$Ph(CH_2)_2$	**1d**	91	(0/40/0/60)
6	*i*-Pr	**1e**	98	(0/28/0/72)
7	*c*-Hex	**1f**	95	(0/28/0/72)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR. c) Unidentified products were formed.



	$J_{Ha\text{-}Hb}$	$J_{Hb\text{-}Hc}$
2	4.0 Hz	2.5 Hz
3	3.5 Hz	6.0 Hz

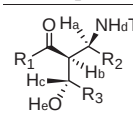
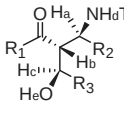
Scheme 3.

The relative configurations at newly created stereo-centers of the β-amino–β'-hydroxy ketones were determined by chemical transformation and NOE experiments (Scheme 3). Namely, treatment of *syn*,*anti*-**1d** and *anti*,*anti*-**1d** with triphosgene in pyridine afforded the carbamates **2** and **3**, which were analyzed by NOE difference spectroscopy. The NOEs between Ha and Hb, Hb and methyl proton, and Ha and methyl proton of **2** clearly indicated the *syn*,*anti* configuration. Similarly, the NOEs between Ha and Hb, Hb and Hc, and Ha and Hc of **3** clearly indicated the *anti*,*anti* configuration. The relative configurations of other products were deduced by comparison of their ^{1}H NMR and ^{13}C NMR spectra with those of *syn*,*anti*-**1d** and *anti*,*anti*-**1d** (Table 2).

Next, the SmI_2-mediated aldol reactions of various aziridinyl ketones with various aldehydes were further examined (Table 3). The reactions between aryl aziridinyl ketones and aldehydes in the presence of SmI_2 also proceeded smoothly to afford the corresponding β-amino–β'-hydroxy ketones (**4a**–**8b**) in excellent yields (Entries 1–10). Such results indicated that the substituents at C-3 position (R_2) play an important role in the control of stereoselectivity. When the reactions with aziridinyl ketones **1** and **4** having a primary alkyl substituent (R_2 = Me, *n*-Pr) were tried, mixtures of two diastereomers (*syn*,*anti* isomer (**B**) and *anti*,*anti* isomer (**D**)) were afforded with poor selectivities. Comparison of these observed diastereoselectivities revealed that they were improved when the bulkiness of the aldehyde increased (Table 1 and Table 3, Entries 1 and 2). On the other hand, it is noteworthy that the reactions afforded the corresponding products with high *anti*,*anti* diastereoselectivities irrespective of the structures of aldehydes when aziridinyl ketones **5** and **6** having a bulky substituent (R_2 = *i*-Pr, *t*-Bu) were used (Entries 3–6). In the case of aziridinyl ketone **7** having an aryl group, *anti*,*anti* isomer (**D**) was obtained as a main product along with a small amount of an unidentified *syn*,*syn* isomer (**A**) or *anti*,*syn* isomer (**C**) (Entries 7 and 8). On the other hand, the reactions of unsubstituented aziridinyl ketone **8** with aldehydes gave only *anti* isomers, as expected (Entries 9 and 10). In addition, it is noted that alkyl aziridinyl ketone **9** also reacted with aldehydes to give the corresponding products (**9a**–**9c**) in high yields (Entries 11–13).

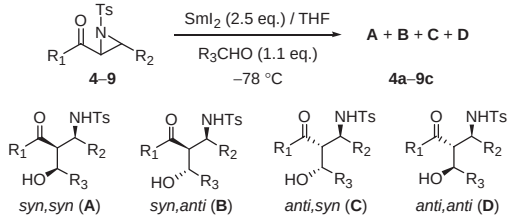
Then, in order to establish the generality of this reaction, we examined the reaction of aziridinyl ketones having other nitro-

Table 2. Chemical Shifts (H_a, H_b, H_c, H_d, H_e, $C_{carbonyl}$) and Coupling Constants (J_{ab}, J_{bc}, J_{ad}, J_{ce}) for β-Amino–β'-Hydroxy Ketones

Compound		δ (H_a)	δ (H_b)	δ (H_c)	δ (H_d)	δ (H_e)	δ ($C_{carbonyl}$)	J_{ab}/Hz	J_{bc}/Hz	J_{ad}/Hz	J_{ce}/Hz
	**1a**	3.80	4.02	5.32	5.22	3.80	202.1	6.9	4.3	8.4	ND[a]
	1c	3.95	3.54	4.01	5.45	3.48	202.4	6.3	2.7	8.6	9.1
	1d	3.94	3.51	4.16	5.47	3.67	202.4	6.6	2.5	8.6	9.2
	1e	3.91	3.66	3.66	5.63	3.66	202.9	6.8	—[b]	8.4	—[b]
syn,anti (**B**)	**1f**	3.91	3.64	3.72	5.72	3.68	202.7	7.0	2.2	8.6	8.0
	**1a**	3.61	3.94	5.20	5.74	2.80	204.2	4.3	7.4	9.0	ND[a]
	1c	3.83	3.64	3.88	5.67	2.69	205.0	5.8	5.8	9.0	7.1
	1d	3.87	3.64	4.05	5.57	2.89	204.8	5.6	5.6	9.2	8.1
	1e	3.79	3.73	3.79	5.73	2.80	205.5	5.5	5.5	8.4	7.2
anti,anti (**D**)	**1f**	3.70	3.82	3.73	5.72	2.75	205.5	5.9	5.3	8.6	7.7

a) Not detected. b) Signals overlapped.

Table 3. The SmI_2-Mediated Aldol Reaction of Various Aziridinyl Ketones with Various Aldehydes



Entry	Aziridinyl ketone			Aldehyde	Product	Yield/%[a]	(**B**/**D**/others)[b]
		R_1	R_2	R_3			
1	**4**	Ph	*n*-Pr	$Ph(CH_2)_2$	**4a**	88	(29/71/0)
2		Ph	*n*-Pr	*i*-Pr	**4b**	92	(14/86/0)
3	**5**	Ph	*i*-Pr	$Ph(CH_2)_2$	**5a**	98	(<5/>95/0)
4		Ph	*i*-Pr	*i*-Pr	**5b**	99	(<5/>95/0)
5	**6**	Ph	*t*-Bu	$Ph(CH_2)_2$	**6a**	96	(<5/>95/0)
6		Ph	*t*-Bu	*i*-Pr	**6b**	99	(<5/>95/0)
7	**7**	Ph	Ph	$Ph(CH_2)_2$	**7a**	96	(28/55/7)
8		Ph	Ph	*i*-Pr	**7b**	97	(13/71/6)
9	**8**	Ph	H	$Ph(CH_2)_2$	**8a**	86	—[c]
10		Ph	H	*i*-Pr	**8b**	83	—[c]
11	**9**	Me	Ph	Ph	**9a**	73	(70/30/0)
12		Me	Ph	$Ph(CH_2)_2$	**9b**	88	(38/62/0)
13		Me	Ph	*i*-Pr	**9c**	99	(29/71/0)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR. c) The *anti* isomer was only obtained.

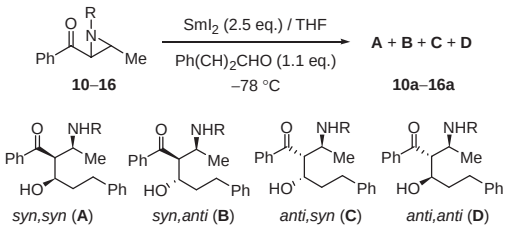
gen protecting groups with 3-phenylpropanal (Table 4). All entries afforded the corresponding β-amino–β'-hydroxy ketones (**10a**–**16a**) in high yields, indicating that this reaction is tolerant of a variety of nitrogen-protecting groups. It was found that the stereoselectivity of this reaction was influenced by the nitrogen-protecting groups. When acetyl (Ac), *t*-butoxycarbonyl (Boc), benzyloxycarbonyl (Cbz), and 9-fluorenylmethoxycarbonyl (Fmoc) were used as nitrogen-protecting groups, the high diastereoselectivities were observed (Entries 3, 5–7). It is noteworthy that the reaction proceeded smoothly in a high yield with excellent diastereoselectivity to give only *anti*,*anti* isomer (**D**) in the case when Fmoc was used as a protecting group (Entry 7).

Since it was found that Fmoc was the most appropriate nitrogen-protecting group in the reaction with 3-phenylpropanal, the SmI_2-mediated aldol reactions of various Fmoc-aziridinyl ketones with various aldehydes were examined; the products were obtained in good to high yields (Table 5). It was also found that the substituents at C-3 position (R_2) play an important role in control of the stereoselectivity. Contrary to the case of using Ts as a protecting group, the reactions with aziridinyl ketones **16** and **17** having a primary alkyl substituent (R_2 = Me, *n*-Pr) afforded the *anti*,*anti* isomers (**D**) with high diastereoselectivities irrespective of the structures of aldehydes (Entries 1–5), and the reactions with aziridinyl ketones having a bulky substituent (R_2 = *i*-Pr) gave mixtures of two diastereomers with poor selectivities in lower yields (Entries 6 and 7). In addition, the reactions with aziridinyl ketone having an aryl substituent afforded mixtures of two diastereomers with moderate selectivity (Entries 8 and 9). These results are in contrast to those of the reactions with tosylaziridinyl ketones.

As described above, it was found that *anti*,*anti*-β-amino–β'-hydroxy ketone was selectively obtained by choosing the appropriate nitrogen-protecting group depending on the substituent at the C-3 position of aziridinyl ketone (Table 6).

Next, the aldol reaction of a chiral aziridinyl ketone with aldehyde was tried in the presence of SmI_2. It was considered that this reaction becomes synthetically more useful when this aldol reaction is applied to an enantiomeric case. The chiral N–H aziridinyl ketone **22** (96% ee by HPLC analysis) was prepared according to the literature procedure.[13] Then, aziridine **22** was treated with tosyl chloride (TsCl) and (4-dimethylamino)pyridine (DMAP) to afford chiral *N*-tosylaziridinyl ketone **5** (Scheme 4).

Table 4. The SmI_2-Mediated Aldol Reaction of Aziridinyl Ketones Having Various Protecting Groups with 3-Phenylpropanal



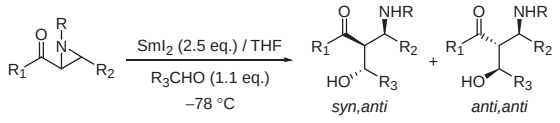
Entry	Aziridine		Product	Yield/%[a]	(**A**/**B**/**C**/**D**)[b]
		R			
1	**10**	Ms	**10a**	96	(0/29/0/71)
2	**11**	Mts[c]	**11a**	96	(0/42/0/58)
3	**12**	Ac	**12a**	85	(0/10/0/90)
4	**13**	Bz	**13a**	82	(0/34/0/66)
5	**14**	Boc	**14a**	93	(0/12/0/88)
6	**15**	Cbz	**15a**	88	(0/<5/0/>95)
7	**16**	Fmoc	**16a**	94	(0/<5/0/>95)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR. c) Mts:2,4,6-trimethylbenzenesulfonyl.

Treatment of the mixture of the optically active ketone (2*S*,3*R*)-**5** and 3-phenylpropanal in THF with THF solution of SmI_2 at -78 °C gave the corresponding β-amino–β'-hydroxy ketone **5a** in high yield with high diastereoselectivity (*syn*,*anti*/*anti*,*anti* = 3/97) (Scheme 5). It was noteworthy that the excellent optical purity of the β-amino–β'-hydroxy ketone **5a** produced was kept throughout the present protocol (96% ee (*anti*,*anti* isomer) by HPLC analysis). In the case of the reaction with isobutyraldehyde, the product was also obtained in a high yield with a high diastereoselectivity (*syn*, *anti*/*anti*,*anti* = 3/97, 96% ee).

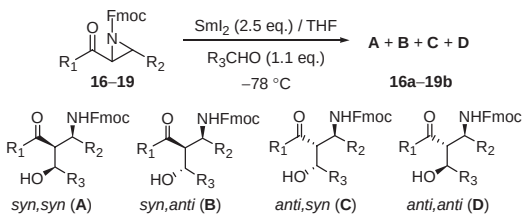
One possible reaction mechanism is shown in Scheme 6. The reaction is assumed to proceed via successive one-electron transfer from SmI_2 to the ketone, followed by opening of the aziridine ring to afford the corresponding β-amino samarium enolate.[5] The formation of a chelated structure is considered to be crucial for the initial electron transfer[4a,14] because simple ketones are not reduced by SmI_2 in THF at -78 °C. Additionally, this consideration can explain the observation that aziridinyl ketones are more quickly reduced compared with coexisting aldehydes. Condensation with an aldehyde then produced the desired β-amino–β'-hydroxy ketone. The stereoselectivity attained in the aldol reaction can be explained reasonably by considering the six-membered boat-like transi-

Table 6. The SmI_2-Mediated Diastereoselective Aldol Reaction



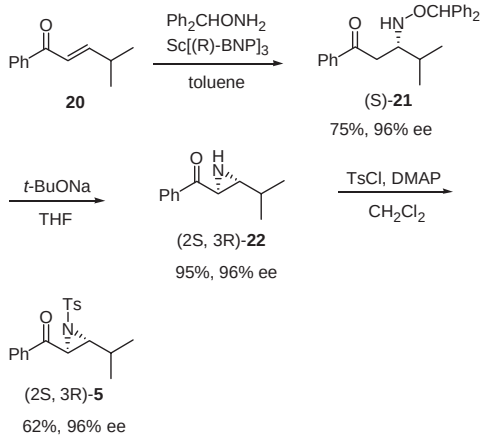
R_2	R	*syn*,*anti*/*anti*,*anti*
alkyl (primary)	Fmoc	1/5–1/>20
alkyl (secondary, tertiary)	Ts	1/>20
aryl	Fmoc	1/2–1/9

Table 5. The SmI_2-Mediated Aldol Reaction of Fmoc-Aziridinyl Ketones with Various Aldehydes

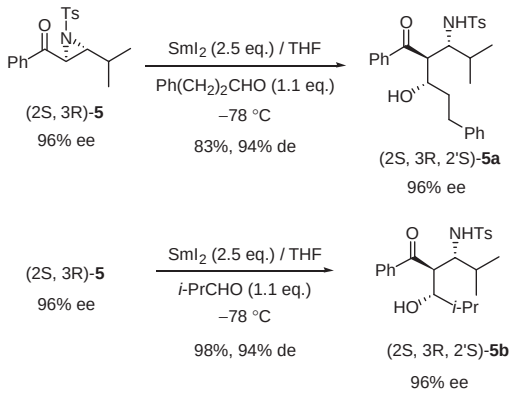


Entry	Azyridinyl ketone			Aldehyde	Product	Yield/%[a]	(**A**/**B**/**C**/**D**)[b]
		R_1	R_2	R_3			
1[c]	**16**	Ph	Me	$Ph(CH_2)_2$	**16a**	94	(0/<5/0/>95)
2		Ph	Me	Ph	**16b**	67	(0/<5/0/>95)
3		Ph	Me	*i*-Pr	**16c**	92	(0/<5/0/>95)
4	**17**	Ph	*n*-Pr	$Ph(CH_2)_2$	**17a**	93	(0/18/0/82)
5		Ph	*n*-Pr	*i*-Pr	**17b**	96	(0/<5/0/>95)
6	**18**	Ph	*i*-Pr	$Ph(CH_2)_2$	**18a**	84	(0/63/0/37)
7		Ph	*i*-Pr	*i*-Pr	**18b**	72	(0/42/0/58)
8	**19**	Ph	Ph	$Ph(CH_2)_2$	**19a**	81	(0/32/0/68)
9		Ph	Ph	*i*-Pr	**19b**	76	(0/9/0/91)

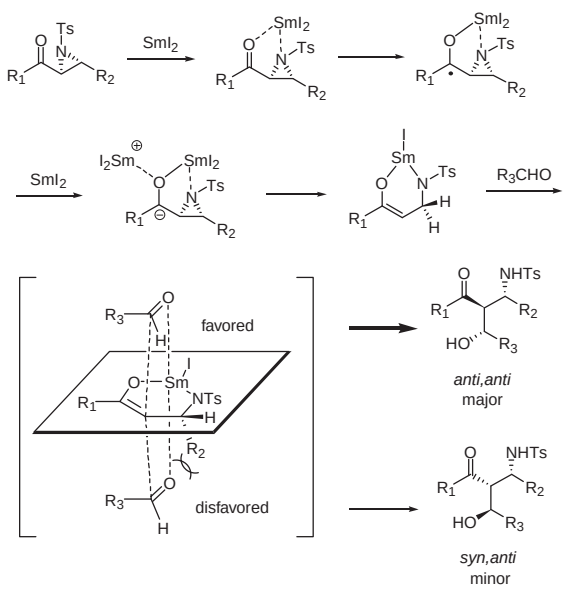
a) Isolated yield. b) The ratio was determined by ^{1}H NMR. c) The result of Table 4, Entry 7.



Scheme 4.

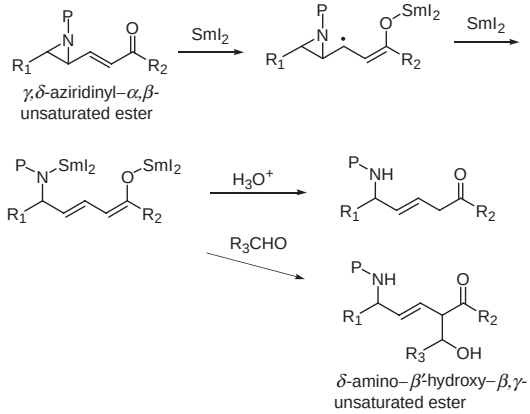


Scheme 5.



Scheme 6. The possible reaction mechanism.

tion state, in which the samarium enolate possessed (*Z*)-configuration by chelation of samarium between the amino group and the carbonyl, and the diastereofacial selectivity was determined by R_2 group.[15] Thus, this aldol reaction afforded the *anti*,*anti*-β-amino–β'-hydroxy ketone as a main product.



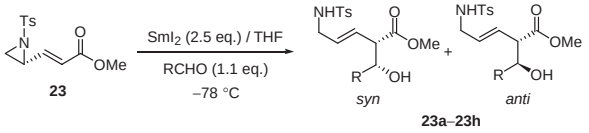
Scheme 7.

Stereoselective Synthesis of δ-Amino–β′-Hydroxy–β,γ-Unsaturated Esters by the Samarium(II) Iodide-Mediated Aldol Reaction of γ,δ-Aziridinyl–α,β-Unsaturated Esters with Aldehydes.[16] Next, in order to extend the generality of this SmI_2-mediated aldol reaction, the uses of γ,δ-aziridinyl–α,β-unsaturated esters instead of the above-mentioned aziridinyl ketones were studied. Thus formed aldol adducts were considered to be δ-amino–β'-hydroxy–β,γ-unsaturated esters (Scheme 7).

The replacement of an amide bond in bioactive peptides with a *trans*-double bond has long been a topic of interests in biological, theoretical, and synthetic areas.[17] δ-Amino–β'-hydroxy–β,γ-unsaturated esters[18] have been considered as important analogues of dipeptide and are expected to be used for synthetic building blocks of various biologically important polypeptides. Now, a new and efficient method for the stereoselective synthesis of δ-amino–β'-hydroxy–β,γ-unsaturated esters has been reported.[16]

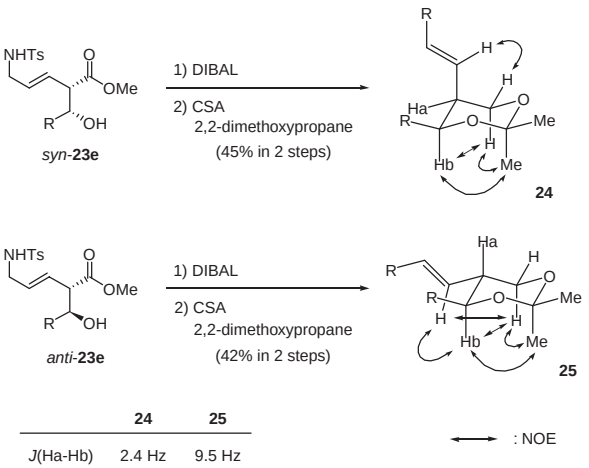
The γ,δ-aziridinyl–α,β-unsaturated esters were prepared according to the literature procedure.[19] In the first place, SmI_2-mediated aldol reaction of methyl (2*E*)-3-[(2*R*)-1-tosylaziridin-2-yl]acrylate (**23**)[19] with several aldehydes was examined (Table 7). The reaction of **23** with benzaldehyde was carried out at -78 °C in THF by adding a THF solution of SmI_2; the corresponding δ-amino–β'-hydroxy–β,γ-unsaturated ester (**23a**) (27/73 mixture of *syn* and *anti* isomers) was obtained in a good yield, along with a small amount of δ-*N*-tosylamino-β,γ-unsaturated methyl ester (Entry 1). The yield of **23a** slightly decreased because the reduction of benzaldehyde took place competitively. Contrary to the reaction with aziridinyl ketones, the reaction with γ,δ-aziridinyl–α,β-unsaturated esters afforded the corresponding products in good yields, irrespective of the aromatic aldehydes having an electron-withdrawing group or an electron-donating group on the aromatic ring (Entries 2 and 3). This result was explained by the difference between reduction rates of γ,δ-aziridinyl–α,β-unsaturated esters and aziridinyl ketones. Further, the reaction of **23** with aliphatic aldehydes proceeded very rapidly to give the corresponding δ-amino–β'-hydroxy–β,γ-unsaturated esters (**23d**–**23h**) in excellent yields (Entries 4–8). It is noted that no olefinic isomers and dienes were detected in this reaction. It is quite clear that nearly neutral conditions are kept during the reaction; therefore the isomerization to a more stable ole-

Table 7. The SmI_2-Mediated Aldol Reaction of γ,δ-Aziridinyl–α,β-Unsaturated Ester (**1**) with Various Aldehydes



Entry	Aldehyde R	Product	Yield/%[a]	(*syn*/*anti*)[b]
1	Ph	**23a**	63	(27/73)
2	4-$MeOC_6H_4$	**23b**	95	(49/51)
3	4-ClC_6H_4	**23c**	75	(39/61)
4	Et	**23d**	92	(55/45)
5	$Ph(CH_2)_2$	**23e**	96	(51/49)
6	*i*-Pr	**23f**	86	(56/44)
7	*c*-Hex	**23g**	94	(54/46)
8	*t*-Bu	**23h**	97	(57/43)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR.



Scheme 8.

finic isomer or β-elimination was prevented. A characteristic point of this aldol reaction is that it proceeded with complete α-regioselectivity and formed (*E*)-olefin selectively, whereas no diastereoselectivity was observed (*syn*/*anti* = 27/73–57/43).

The (*E*)-olefin stereochemistry of **23e** was assigned based on the relevant vicinal coupling constant (J = 15.7 Hz). The relative configuration at newly created stereo-centers of **23e** was determined by chemical transformation and measurement of the coupling constants of their acetonide derivatives (Scheme 8). Namely, reduction of *syn*-**23e** and *anti*-**23e** with diisobutylaluminium hydride (DIBAL) afforded the diols, which converted to the corresponding acetonide derivatives **24** and **25**. The observation of an equatorial–axial coupling constant (J = 2.4 Hz) between Ha and Hb in the ^{1}H NMR data of **24** indicated that **24** has *syn* configuration. On the other hand, the observation of a diaxial coupling constant (J = 9.5 Hz) between Ha and Hb in the ^{1}H NMR data of **25** indicated that **25** has *anti* configuration. The relative configurations of other products were deduced by comparison of their ^{1}H NMR and ^{13}C NMR spectra with those of *syn*-**23e** and *anti*-**23e** (Table 8).

Table 8. Chemical Shifts (H_a, H_b) and Coupling Constants (J_{ab}) for δ-Amino–β'-Hydroxy–β,γ-Unsaturated Esters

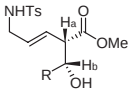
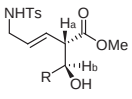
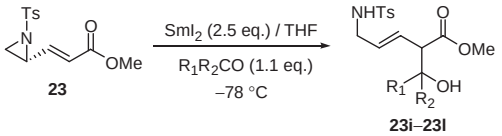
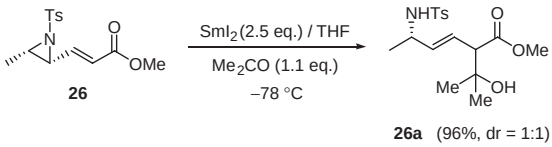
Compound		δ (H_a)	δ (H_b)	J_{ab}/Hz
	**23a**	3.26	5.02	5.4
	23d	3.02	3.80	4.3
	23e	3.01	3.89	4.3
	23f	3.18	3.63	4.3
	23g	3.21	3.61	4.6
	23h	3.24	3.62	4.9
	**23a**	3.34	4.84	8.1
	23d	3.07	3.65	7.6
	23e	3.07	3.74	7.3
	23f	3.18	3.50	7.8
	23g	3.23	3.47	7.8
	23h	3.26	3.52	0

Table 9. The SmI_2-Mediated Aldol Reaction of γ,δ-Aziridinyl–α,β-Unsaturated Ester (**23**) with Various Ketones



Entry	Ketone R_1	Ketone R_2	Product	Yield/%[a]	(Diastereomeric ratio)
1	$Ph(CH_2)_2$	Me	**23i**	98	(56/44)[b]
2	Me	Me	**23j**	94	—
3	Et	Et	**23k**	87	—
4	$-(CH_2)_5-$		**23l**	95	—

a) Isolated yield. b) The stereochemistries were not determined.



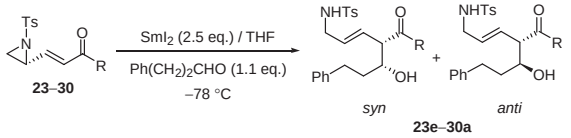
Scheme 9.

Next, the possible applications of this aldol reaction to ketones were examined. Then, the reaction also proceeded smoothly to afford the corresponding δ-amino–β'-hydroxy–β,γ-unsaturated esters (**23i–23l**) in high yields (Table 9).

The product **26a** was obtained in a high yield by the reaction of **26** with acetone, however, almost no stereoselectivity was observed (Scheme 9). It seems that the distal substituent on the δ-carbon has no stereodirecting effect concerning the incoming electrophile.

Next, the aldol reaction was examined by using other aziridinyl unsaturated esters in order to improve the diastereoselectivity (Table 10). In this reaction, the bulkiness of the R group did not influence on the reactivity, and the products were obtained in high yields. Comparison of the observed diastereoselectivities revealed that some bulkiness of the R group would be crucial to achieve good stereoselectivity. In particularly, high *syn* diastereoselectivity (*syn*/*anti* = 90/10) was observed

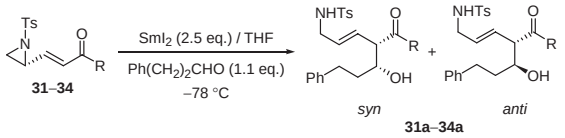
Table 10. The SmI_2-Mediated Aldol Reaction of Various Unsaturated Aziridines with 3-Phenylpropanal



Entry	Aziridine	R	Product	Yield/%[a]	(*syn*/*anti*)[b]
1	**23**	OMe	**23e**	96	(51/49)
2	**27**	OBn	**27a**	99	(70/30)
3	**28**	O-*t*-Bu	**28a**	98	(71/29)
4	**29**	OPh	**29a**	95	(73/27)
5	**30**	O-2,6-diMe-Ph	**30a**	97	(90/10)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR.

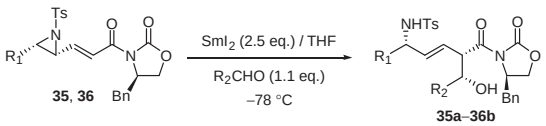
Table 11. The SmI_2-Mediated Aldol Reaction of Various Unsaturated Aziridines with 3-Phenylpropanal



Entry	Aziridne	R	Product	Yield/%[a]	(*syn*/*anti*)[b]
1	**31**	Ph	**31a**	61	(58/42)
2	**32**	NEt_2	**32a**	83	(60/40)
3	**33**	pyrrolidine	**33a**	82	(47/53)
4	**34**	2-oxazolidinone	**34a**	81	(>95/<5)

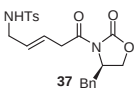
a) Isolated yield. b) The ratio was determined by ^{1}H NMR.

Table 12. The Asymmetric SmI_2-Mediated Aldol Reaction



Entry	Aziridine	R_1	R_2	Product	Yield/%[a]	(*syn*/*anti*)[b]
1	**35**	H	$Ph(CH_2)_2$	**35a**	93	(>95/<5)
2		H	Et	**35b**	85	(>95/<5)
3		H	*i*-Pr	**35c**	81	(>95/<5)
4		H	*c*-Hex	**35d**	77	(>95/<5)
5		H	*t*-Bu		ND[c]	
6		H	Ph		ND[d]	
7	**36**	Me	$Ph(CH_2)_2$	**36a**	86	(>95/<5)
8		Me	*i*-Pr	**36b**	76	(>95/<5)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR. c) **37** was obtained in 85% yield. d) **37** was obtained in 82% yield.



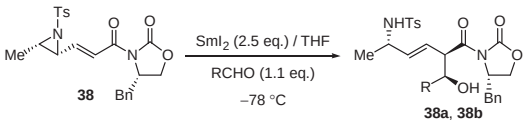
when 2,6-dimethylphenyl ester **30** was used (Entry 5).

Then, the aldol reaction was examined by using other unsaturated aziridines (ketone, amide, and imide) in order to establish the generality of this reaction (Table 11). Reactions between other unsaturated aziridines and 3-phenylpropanal also proceeded smoothly and afforded the corresponding δ-amino–β'-hydroxy–β,γ-unsaturated carbonyl compounds (**31a**–**34a**) in high yields. It is noted that an excellent *syn* diastereoselectivity was observed (*syn*/*anti* = >95/<5) when unsaturated imide **34** was used (Entry 4).

Prompted by this result, we applied the aldol reaction to the asymmetric one[20] by introducing a chiral 2-oxazolidinone auxiliary[21] to the unsaturated aziridine with the expectation that it would control the stereochemistry. In the first place, the reaction of (4*R*)-4-benzyl-3-[(2*E*)-3-((2*R*)-1-tosylaziridin-2-yl)-acryloyl]oxazolidin-2-one (**35**) with 3-phenylpropanal was examined (Table 12, Entry 1). This asymmetric aldol reaction proceeded smoothly and afforded the corresponding product **35a** in high yield with excellent *syn* diastereoselectivity (*syn*/*anti* = >95/<5) and high diastereofacial selectivity (>95/<5 for *syn*-isomer). Further, the corresponding products (**35b**–**35d**) were also obtained in high yields with excellent diastereoselectivities (*syn*/*anti* = >95/<5) and high diastereofacial selectivities (>95/<5 for *syn*-isomers) when other aldehydes were used (Entries 2–4). In this reaction, the major isomers were formed with >95% diastereoselection, as judged by the analysis of the ^{1}H NMR measurements. With bulky aldehyde, however, such as pivalaldehyde, no aldol adduct was obtained and the reduction product **37** resulted (Entry 5). In the case of using benzaldehyde, no aldol adduct was obtained because one-electron reduction of benzaldehyde preferentially causes its pinacol coupling (Entry 6). As described above, the 2-oxazolidinone auxiliary exhibited excellent ability for stereocontrol in the asymmetric SmI_2-mediated aldol reaction.

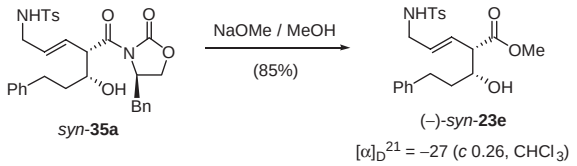
Next, the reaction of (4*R*)-4-benzyl-3-[(2*E*)-3-((2*R*,3*S*)-3-methyl-1-tosylaziridin-2-yl)acryloyl]oxazolidin-2-one (**36**) (Table 12, Entries 7, 8) and (4*S*)-4-benzyl-3-[(2*E*)-3-((2*R*,3*S*)-3-methyl-1-tosylaziridin-2-yl)acryloyl]oxazolidin-2-one (**38**)

Table 13. The Asymmetric SmI_2-Mediated Aldol Reaction



Entry	R	Product	Yield/%[a]	(*syn*/*anti*)[b]
1	$Ph(CH_2)_2$	**38a**	84	(>95/<5)
2	*i*-Pr	**38b**	75	(>95/<5)

a) Isolated yield. b) The ratio was determined by ^{1}H NMR.



Scheme 10.

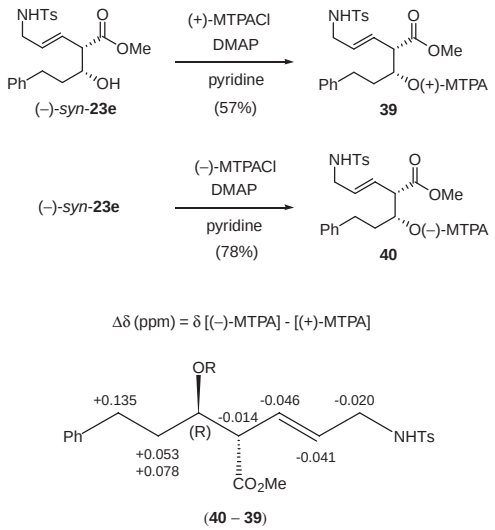
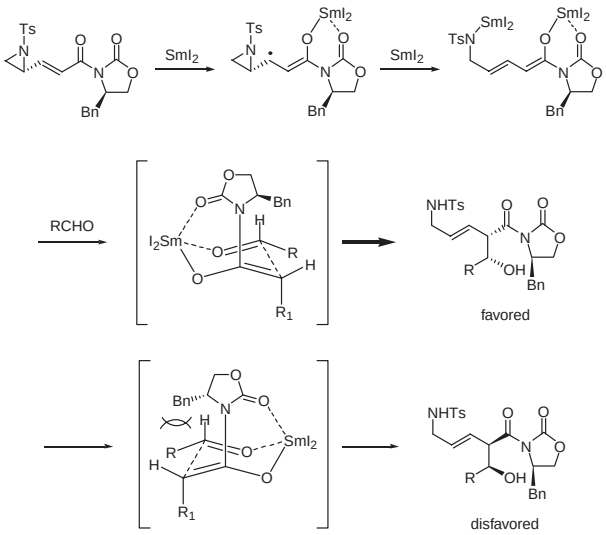


Fig. 1. Application of the modified Mosher method.

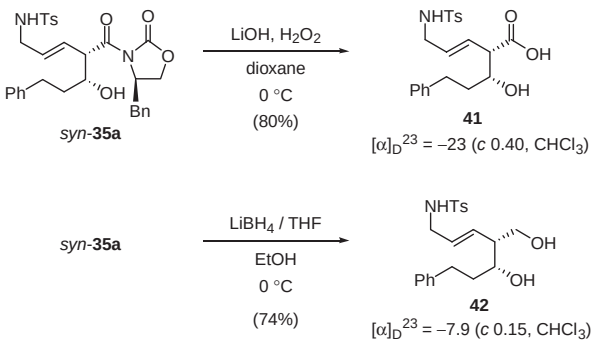
(Table 13) with aldehydes was further tried. The products were obtained in high yields with high diastereoselectivities (*syn*/*anti* = >95/<5) and high diastereofacial selectivities (>95/<5 for *syn*-isomers). Similar to the case of the reaction with methyl ester **26** (Scheme 9), it was considered that the distal substituent on the δ-carbon has no stereodirecting effect with respect to the incoming aldehyde.

The relative stereochemistry of *syn*-**35a** was assigned by converting to its structurally-defined methyl ester (−)-*syn*-**23e** by methanolysis (Scheme 10). And the absolute configuration of (−)-*syn*-**23e** was determined by the modified Mosher method.[22] Namely, (−)-*syn*-**23e** was treated with (+)- and (−)-α-methoxy–α-trifluoromethylphenylacetyl (MTPA) chloride to give the (+)- and (−)-MTPA esters (**39** and **40**) and comparison of the ^{1}H NMR data of **39** and **40** indicated that the absolute configuration of β'-position of the carbonyl group is (*R*)-configuration (Fig. 1).

A reaction mechanism that can rationalize these observations is shown in Scheme 11. The first step of this reaction involves reduction of the aziridinyl unsaturated imide via successive one-electron transfer from SmI_2 to cause both fragmentation of an aziridine ring and migration of a double bond. Then, the samarium imide enolate[6,18,23] was formed which in turn nucleophilically attacks the aldehyde. The samarium would play an important role in the transition state of the reaction for inducing a high diastereoselectivity. Namely, the stereoselectivity of the reaction is explained by the chelated six-membered transition state model in which both the aldehyde and the oxazolidinone carbonyl are coordinated to samarium[20,24] and the diastereofacial selectivity was produced by the steric effect of benzyl group of oxazolidinone.



Scheme 11. The assumed reaction mechanism.



Scheme 12.

Finally, the transformation of these aldol adducts to carboxylic acid and alcohol was tried. As shown in Scheme 12, *syn*-**35a** was converted to carboxylic acid **41** in 80% yield on treatment with LiOH and H_2O_2, while alcohol **42** was given in 74% yield on treatment with $LiBH_4$.[25] In these reactions, no detectable epimerization nor double bond conjugation was observed.

Conclusion

The samarium(II) iodide-mediated aldol reactions of acylaziridines with aldehydes were developed. β-Amino–β'-hydroxy ketones were synthesized in high yields by the aldol reaction of aldehydes with samarium enolates generated by aziridine-fragmentation of aziridinyl ketones with two moles of samarium(II) iodide. By choice of appropriate nitrogen-pro-

tecting groups of aziridinyl ketones, depending on the substituent at C-3 position of aziridinyl ketone, *anti*,*anti*-β-amino–β'-hydroxy ketones were diastereoselectively obtained among the four possible diastereomers. Furthermore, enantiomerically pure *anti*,*anti*-β-amino–β'-hydroxy ketones were successfully obtained by this aldol reaction with chiral aziridinyl ketones. δ-Amino–β'-hydroxy–β,γ-unsaturated esters were also synthesized in high yields by the aldol reaction of aldehydes with samarium enolates generated by aziridine-fragmentation and olefin-migration of γ,δ-aziridinyl–α,β-unsaturated esters using two moles of samarium(II) iodide. This aldol reaction proceeded with complete α-regioselectivity and selectively formed (*E*)-olefin. By introducing chiral 2-oxazolidinone auxiliary to γ,δ-aziridinyl–α,β-unsaturated esters, we applied this reaction successfully to the asymmetric reaction; enantiomerically pure *syn*-δ-amino–β'-hydroxy–β,γ-unsaturated esters were obtained in high yields.

Experimental

General. Infrared (IR) spectra were recorded on a JASCO FT-IR-8900 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on EX270L (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$; $\delta = 77.0$ ppm). The optical rotations were measured with a JASCO P-1020 polarimeter. High-resolution mass spectra (HRMS) were recorded on a JMS-700 mass spectrometer. Analytical TLC was performed on Merck preparative TLC plates (silica gel 60 GF254, 0.25 mm). Column chromatography was carried out on Merck silica gel 60 (0.063–0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. All reactions were carried out under an argon atmosphere in dried glassware, unless otherwise noted. Dry solvents were prepared by distillation under appropriate drying agents. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Kokusan Chemical, Wako Pure Chemical Industries, or Aldrich Chemical. Samarium iodide THF solution (0.1 M) was prepared from samarium metal and diiodomethane according to the literature method.[26] Aldehydes were used after purification by distillation or recrystallizaion.

***trans*-2-Benzoyl-3-methyl-1-tosylaziridine (1).** To a suspension of 1-phenyl-2-buten-1-one (2.74 g, 18.8 mmol) and PhI=NTs (1.40 g, 3.75 mmol) in dry CH_3CN (50 mL) at room temperature under an argon atmosphere was added [Cu(acac)$_2$] (98 mg, 0.38 mmol). After the reaction mixture was stirred for 4 h, the reaction mixture was filtered through a short pad of silica gel with EtOAc as eluent. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-3-methyl-1-tosylaziridine (**1**) (709 mg, 60%). IR (neat) 1690, 1326, 1162 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.2$ Hz, 2H), 7.84 (d, $J = 8.2$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.6$ Hz, 2H), 4.16 (d, $J = 3.9$ Hz, 1H), 3.25 (dq, $J = 3.9$, 5.9 Hz, 1H), 2.35 (s, 3H), 1.82 (d, $J = 5.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.2, 144.1, 136.6, 135.3, 133.7, 129.3, 128.5, 128.2, 127.1, 46.8, 45.2, 21.5, 13.6. HRMS (ESI) calcd for $C_{17}H_{18}NO_3S$ $[M + H]^+$ 316.1007, found 316.1001.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of Aziridinyl Ketone with Aldehyde. (Table 1, Entry 5). To a mixture of aziridinyl ketone **1** (51.5 mg, 0.162 mmol) and 3-phenylpropanal (23.9 mg, 0.178 mmol) in THF (4 mL) at -78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 4.05 mL, 0.405 mmol). After the reaction mixture was stirred for 1 h at -78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford *syn*,*anti*-**1d** (26.6 mg, 36%) and *anti*,*anti*-**1d** (39.8 mg, 54%), respectively.

***syn*,*anti*-1a:** Colorless oil. IR (neat) 3491, 3265, 1666, 1328, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.68–7.59 (m, 4H), 7.44 (t, $J = 8.1$ Hz, 1H), 7.27–7.11 (m, 9H), 5.32 (d, $J = 4.3$ Hz, 1H), 5.22 (d, $J = 8.4$ Hz, 1H), 4.02 (dd, $J = 6.9$, 4.8 Hz, 1H), 4.00–3.73 (m, 2H), 2.39 (s, 3H), 1.01 (d, $J = 4.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.1, 143.4, 141.4, 137.5, 137.1, 133.2, 129.6, 128.5, 128.3, 128.3, 127.4, 127.0, 125.8, 72.7, 57.2, 50.1, 21.5, 19.8. HRMS (ESI) calcd for $C_{24}H_{26}NO_4S$ $[M + H]^+$ 424.1583, found 424.1564.

***anti*,*anti*-1a:** Colorless oil. IR (neat) 3486, 3324, 1650, 1332, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.7$ Hz, 2H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.56 (t, $J = 8.3$ Hz, 1H), 7.53–7.23 (m, 9H), 5.74 (d, $J = 9.0$ Hz, 1H), 5.20 (d, $J = 7.4$ Hz, 1H), 3.94 (dd, $J = 7.4$, 4.3 Hz, 1H), 3.66–3.55 (m, 1H), 2.80 (brs, 1H), 2.41 (s, 3H), 0.96 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.2, 143.0, 141.4, 138.6, 138.2, 133.5, 129.4, 128.5, 128.5, 128.3, 128.1, 126.6, 126.3, 74.1, 56.3, 50.0, 21.5, 20.4. HRMS (ESI) calcd for $C_{24}H_{26}NO_4S$ $[M + H]^+$ 424.1583, found 424.1580.

***anti*,*anti*-1b:** Colorless oil. IR (neat) 3490, 3310, 1664, 1250, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.7$ Hz, 2H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.55 (t, $J = 8.3$ Hz, 1H), 7.43 (t, $J = 8.3$ Hz, 2H), 7.36–7.16 (m, 4H), 6.84 (d, $J = 8.3$ Hz, 2H), 5.85 (d, $J = 8.9$ Hz, 1H), 5.15 (d, $J = 7.8$ Hz, 1H), 3.89 (dd, $J = 7.8, 3.8$ Hz, 1H), 3.80 (s, 3H), 3.58–3.47 (m, 1H), 2.63 (brs, 1H), 2.40 (s, 3H), 0.91 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.6, 159.3, 143.0, 138.8, 138.3, 133.6, 133.5, 129.5, 128.5, 128.4, 127.7, 126.7, 113.8, 73.8, 56.4, 55.2, 49.9, 21.6, 20.5. HRMS (ESI) calcd for $C_{25}H_{27}NNaO_5S$ $[M + Na]^+$ 476.1508, found 476.1517.

***syn*,*anti*-1c:** Colorless oil. IR (neat) 3484, 3265, 1666, 1328, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.77 (d, $J = 8.7$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 8.4$ Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 2H), 7.19 (d, $J = 8.7$ Hz, 2H), 5.45 (d, $J = 8.6$ Hz, 1H), 4.00–3.89 (m, 2H), 3.56–3.45 (m, 2H), 2.38 (s, 3H), 1.38 (qd, $J = 7.3$, 5.1 Hz, 2H), 1.15 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.4, 143.1, 137.6, 137.0, 133.6, 129.5, 128.6, 128.2, 126.9, 72.4, 53.8, 50.6, 29.1, 21.6, 20.9, 10.9. HRMS (ESI) calcd for $C_{20}H_{26}NO_4S$ $[M + H]^+$ 376.1583, found 376.1586.

***anti*,*anti*-1c:** Colorless oil. IR (neat) 3503, 3284, 1662, 1332, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.6$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.56 (t, $J = 8.4$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 8.7$ Hz, 2H), 5.67 (d, $J = 9.0$ Hz, 1H), 3.92–3.65 (m, 2H), 3.64 (t, $J = 5.8$ Hz, 1H), 2.69 (d, $J = 7.1$ Hz, 1H), 2.39 (s, 3H), 1.42 (qd, $J = 7.3$, 4.3 Hz, 2H), 1.05 (d, $J = 6.6$ Hz, 3H), 0.86 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.0, 143.1, 138.2, 138.1, 133.6, 129.5, 128.6,

128.4, 126.8, 73.1, 54.2, 50.2, 28.5, 21.6, 20.6, 10.1. HRMS (ESI) calcd for $C_{20}H_{26}NO_4S$ $[M + H]^+$ 376.1583, found 376.1586.

***syn*,*anti*-1d:** Colorless oil. IR (neat) 3443, 3216, 1664, 1328, 1161 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.6$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 7.56 (t, $J = 8.4$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 2H), 7.26–7.04 (m, 7H), 5.47 (d, $J = 8.6$ Hz, 1H), 4.17–4.12 (m, 1H), 4.07–3.88 (m, 1H), 3.67 (d, $J = 9.2$ Hz, 1H), 3.51 (dd, $J = 6.6$, 2.5 Hz, 1H), 2.83–2.75 (m, 1H), 2.65–2.56 (m, 1H), 2.38 (s, 3H), 1.75–1.58 (m, 2H), 1.11 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.4, 143.1, 141.3, 137.4, 136.9, 133.7, 129.5, 128.6, 128.3, 128.3, 128.2, 126.9, 125.8, 70.3, 54.1, 50.5, 37.7, 32.6, 21.6, 20.9. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1884.

***anti*,*anti*-1d:** Colorless oil. IR (neat) 3495, 3313, 1649, 1332, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.86 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.58 (t, $J = 8.4$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 2H), 7.27–7.08 (m, 7H), 5.57 (d, $J = 9.2$ Hz, 1H), 4.08–4.02 (m, 1H), 3.89–3.82 (m, 1H), 3.64 (t, $J = 5.6$ Hz, 1H), 2.89 (d, $J = 8.1$ Hz, 1H), 2.79–2.72 (m, 1H), 2.60–2.37 (m, 1H), 2.38 (s, 3H), 1.79–1.65 (m, 2H), 1.03 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.8, 143.2, 141.3, 138.0, 137.9, 133.7, 129.5, 128.7, 128.4, 128.3, 128.2, 126.8, 125.8, 71.4, 54.4, 50.3, 37.3, 32.1, 21.6, 20.4. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1892.

***syn*,*anti*-1e:** Colorless oil. IR (neat) 3452, 3216, 1664, 1328, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.2$ Hz, 2H), 7.62–7.54 (m, 3H), 7.42 (t, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 5.63 (d, $J = 8.4$ Hz, 1H), 3.95–3.83 (m, 1H), 3.70–3.64 (m, 3H), 2.37 (s, 3H), 1.66–1.57 (m, 1H), 1.24 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.6$ Hz, 3H), 0.76 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.9, 142.9, 137.7, 136.5, 133.7, 129.3, 128.6, 128.2, 126.9, 76.9, 51.0, 50.3, 33.0, 21.6, 21.0, 19.8, 19.4. HRMS (ESI) calcd for $C_{21}H_{28}NO_4S$ $[M + H]^+$ 390.1739, found 390.1737.

***anti*,*anti*-1e:** Colorless oil. IR (neat) 3456, 3283, 1661, 1332, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.58 (t, $J = 8.4$ Hz, 1H), 7.45 (t, $J = 8.1$ Hz, 2H), 7.25 (t, $J = 8.1$ Hz, 2H), 5.73 (d, $J = 8.4$ Hz, 1H), 3.84–3.70 (m, 3H), 2.80 (d, $J = 7.2$ Hz, 1H), 2.37 (s, 3H), 1.66–1.57 (m, 1H), 1.07 (d, $J = 6.1$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.77 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.5, 143.1, 138.1, 133.6, 129.4, 128.6, 128.4, 126.8, 76.3, 51.3, 50.2, 31.1, 21.5, 20.6, 19.7, 16.6. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_4S$ $[M + Na]^+$ 412.1559, found 412.1550.

***syn*,*anti*-1f:** Colorless oil. IR (neat) 3507, 3237, 1665, 1333, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.61–7.55 (m, 3H), 7.42 (t, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 5.72 (d, $J = 8.6$ Hz, 1H), 3.95–3.86 (m, 1H), 3.77–3.63 (m, 3H), 2.37 (s, 3H), 2.08–2.01 (m, 1H), 1.75–1.58 (m, 2H), 1.47–1.20 (m, 3H), 1.22 (d, $J = 6.1$ Hz, 3H), 1.15–0.84 (m, 5H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.7, 142.7, 137.7, 136.2, 133.5, 129.2, 128.5, 128.1, 126.7, 75.9, 51.0, 49.6, 42.3, 29.9, 29.5, 26.1, 25.8, 25.7, 21.5, 21.1. HRMS (ESI) calcd for $C_{24}H_{32}NO_4S$ $[M + H]^+$ 430.2052, found 430.2044.

***anti*,*anti*-1f:** Colorless oil. IR (neat) 3499, 3304, 1653, 1335, 1164 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.58 (t, $J = 8.2$ Hz, 1H), 7.46 (t, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 5.72 (d, $J = 8.6$ Hz, 1H), 3.85–3.65 (m, 3H), 2.75 (d, $J = 7.7$ Hz, 1H), 2.37 (s, 3H), 1.77–1.58 (m, 4H), 1.29–0.98 (m, 7H), 1.10 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.5, 143.1, 138.1, 133.6, 129.5, 128.7, 128.4, 126.8, 75.6, 50.7, 50.1, 40.9, 29.9, 26.9, 26.3, 26.0, 25.9, 21.6, 20.8. HRMS (ESI) calcd for $C_{24}H_{32}NO_4S$ $[M + H]^+$ 430.2052, found 430.2044.

Carbamate 2. To a solution of *syn*,*anti*-**1d** (22.2 mg, 0.0492 mmol) and pyridine (163 mg, 2.06 mmol) in CH_2Cl_2 (7 mL) was added triphosgene (72.9 mg, 0.246 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford carbamate **2** (21.6 mg, 92%). Colorless oil. IR (neat) 1723, 1679, 1358, 1221 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.76 (d, $J = 6.7$ Hz, 2H), 7.73 (d, $J = 6.6$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 6.3$ Hz, 2H), 7.22–7.02 (m, 5H), 6.95 (d, $J = 6.4$ Hz, 2H), 4.75 (qd, $J = 6.6$, 2.3 Hz, 1H), 4.60 (dt, $J = 9.4$, 3.8 Hz, 1H), 3.66 (t, $J = 3.1$ Hz, 1H), 2.76–2.64 (m, 1H), 2.59–2.46 (m, 1H), 2.37 (s, 3H), 2.01–1.85 (m, 1H), 1.69–1.58 (m, 1H), 1.57 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 196.1, 147.9, 144.7, 139.8, 135.8, 135.2, 134.1, 129.2, 129.1, 128.9, 128.4, 128.3, 128.1, 126.2, 74.7, 53.2, 45.9, 33.6, 31.5, 23.0, 21.8. HRMS (ESI) calcd for $C_{27}H_{28}NO_5S$ $[M + H]^+$ 478.1688, found 478.1681.

Carbamate 3. To a solution of *anti*,*anti*-**1d** (28.8 mg, 0.0638 mmol) and pyridine (212 mg, 2.68 mmol) in CH_2Cl_2 (8 mL) was added triphosgene (94.6 mg, 0.319 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford carbamate **3** (21.4 mg, 70%). Colorless oil. IR (neat) 1730, 1672, 1223 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, $J = 7.3$ Hz, 2H), 7.83 (d, $J = 7.3$ Hz, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.35–7.14 (m, 5H), 6.98 (d, $J = 7.4$ Hz, 2H), 4.82 (quintet, $J = 6.5$ Hz, 1H), 4.58 (dt, $J = 10.0$, 3.8 Hz, 1H), 4.24 (dd, $J = 6.1$, 3.6 Hz, 1H), 2.85–2.72 (m, 1H), 2.68–2.55 (m, 1H), 2.44 (s, 3H), 1.96–1.82 (m, 1H), 1.80–1.65 (m, 1H), 1.43 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 196.4, 149.5, 144.7, 139.6, 137.5, 136.5, 134.0, 129.4, 129.1, 128.6, 128.5, 128.3, 128.0, 126.2, 76.9, 54.9, 47.2, 34.2, 31.6, 21.7, 18.7. HRMS (ESI) calcd for $C_{27}H_{28}NO_5S$ $[M + H]^+$ 478.1688, found 478.1718.

Typical Procedure for the Preparation of *N*-Tosylaziridinyl Ketone. N–H aziridines were prepared from corresponding the α,β-unsaturated ketones according to the literature procedure.[12] To a solution of 2-benzoyl-3-propyl-1*H*-aziridine (480 mg, 2.54 mmol) and DMAP (776 mg, 6.35 mmol) in CH_2Cl_2 (10 mL) was added TsCl (726 mg, 3.81 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-3-propyl-1-tosylaziridine (**4**) (691 mg, 79%).

***trans*-2-Benzoyl-3-propyl-1-tosylaziridine (4):** Colorless oil. IR (neat) 1689, 1328, 1161 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.26 (d, $J = 7.6$ Hz, 2H),

4.11 (d, $J = 4.1$ Hz, 1H), 3.23–3.15 (m, 1H), 2.39 (s, 3H), 2.32–2.15 (m, 1H), 2.10–1.95 (m, 1H), 1.63–1.48 (m, 2H), 0.99 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.4, 144.3, 136.8, 135.6, 133.9, 129.5, 128.7, 128.5, 127.5, 49.8, 46.8, 30.4, 21.7, 21.2, 13.9. HRMS (ESI) calcd for $C_{19}H_{22}NO_3S$ $[M + H]^+$ 344.1320, found 344.1319.

***trans*-2-Benzoyl-3-isopropyl-1-tosylaziridine (5):** Colorless oil. IR (neat) 1685, 1329, 1164 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 7.6$ Hz, 2H), 4.04 (d, $J = 4.1$ Hz, 1H), 3.17 (dd, $J = 8.7$, 4.1 Hz, 1H), 2.31 (s, 3H), 2.15–2.04 (m, 1H), 1.09 (d, $J = 6.4$ Hz, 3H), 1.02 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 190.5, 143.8, 136.2, 135.3, 133.4, 129.0, 128.2, 128.1, 127.1, 54.2, 46.6, 28.5, 21.1, 20.3, 20.1. HRMS (ESI) calcd for $C_{19}H_{22}NO_3S$ $[M + H]^+$ 344.1320, found 344.1305.

***trans*-2-Benzoyl-3-*t*-butyl-1-tosylaziridine (6):** Colorless oil. IR (neat) 1687, 1318, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.6$ Hz, 2H), 3.80 (d, $J = 4.4$ Hz, 1H), 3.47 (d, $J = 4.4$ Hz, 1H), 2.42 (s, 3H), 0.87 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 190.1, 143.9, 136.2, 135.9, 133.4, 129.0, 128.6, 128.2, 127.6, 52.9, 46.7, 30.4, 26.1, 21.4. HRMS (ESI) calcd for $C_{20}H_{23}NNaO_3S$ $[M + Na]^+$ 380.1296, found 380.1281.

***trans*-2-Benzoyl-3-phenyl-1-tosylaziridine (7):** Colorless oil. IR (neat) 1686, 1322, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.04 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.35–7.18 (m, 7H), 4.51 (d, $J = 4.1$ Hz, 1H), 4.28 (d, $J = 4.1$ Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 190.1, 144.2, 136.5, 135.8, 134.0, 132.8, 129.4, 128.8, 128.8, 128.7, 128.5, 127.6, 127.4, 50.2, 47.5, 21.7. HRMS (ESI) calcd for $C_{22}H_{20}NO_3S$ $[M + H]^+$ 378.1164, found 378.1201.

***trans*-2-Benzoyl-1-tosylaziridine (8):** Colorless oil. IR (neat) 1691, 1315, 1233, 1163 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.84 (d, $J = 8.2$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.6$ Hz, 2H), 4.18 (dd, $J = 6.9$, 4.1 Hz, 1H), 2.87 (d, $J = 6.9$ Hz, 1H), 2.71 (d, $J = 4.3$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 190.7, 144.7, 135.0, 133.7, 133.6, 129.4, 128.3, 128.2, 127.6, 37.5, 32.4, 21.2. HRMS (ESI) calcd for $C_{16}H_{16}NO_3S$ $[M + H]^+$ 302.0851, found 302.0863.

***trans*-2-Acetyl-3-phenyl-1-tosylaziridine (9):** Colorless oil. IR (neat) 1725, 1333, 1163 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.69 (d, $J = 8.2$ Hz, 2H), 7.31–7.20 (m, 7H), 4.26 (d, $J = 4.1$ Hz, 1H), 3.73 (d, $J = 4.1$ Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 200.0, 144.2, 136.3, 131.4, 129.4, 128.8, 128.2, 127.8, 127.2, 50.9, 48.6, 28.4, 21.5. HRMS (ESI) calcd for $C_{17}H_{18}NO_3S$ $[M + H]^+$ 316.1007, found 316.0993.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of Aziridinyl Ketone with Aldehyde. (Table 3, Entry 3). To a mixture of *trans*-2-benzoyl-3-isopropyl-1-tosylaziridine (**5**) (60.5 mg, 0.176 mmol) and 3-phenylpropanal (26.0 mg, 0.193 mmol) in THF (4 mL) at -78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 4.4 mL, 0.44 mmol). After the reaction mixture was stirred for 1 h at -78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford *anti*,*anti*-**5a** (78.0 mg, 98%).

***syn*,*anti*-4a:** Colorless oil. IR (neat) 3464, 3222, 1661, 1326, 1154 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70 (d, $J = 8.2$ Hz, 2H), 7.61–7.52 (m, 3H), 7.38 (t, $J = 8.2$ Hz, 2H), 7.26–7.05 (m, 7H), 5.46 (d, $J = 8.6$ Hz, 1H), 4.15–4.02 (m, 1H), 3.87–3.65 (m, 2H), 3.59 (dd, $J = 5.5$, 2.6 Hz, 1H), 2.90–2.75 (m, 1H), 2.68–2.42 (m, 1H), 2.38 (s, 3H), 1.81–1.75 (m, 1H), 1.70–1.47 (m, 3H), 1.27–0.93 (m, 2H), 0.73 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.8, 142.9, 141.3, 137.9, 136.7, 133.7, 129.3, 128.6, 128.3, 128.3, 126.9, 125.8, 70.5, 55.1, 51.5, 38.0, 36.7, 32.5, 21.6, 19.3, 13.7. HRMS (ESI) calcd for $C_{28}H_{34}NO_4S$ $[M + H]^+$ 480.2209, found 480.2217.

***anti*,*anti*-4a:** Colorless oil. IR (neat) 3484, 3294, 1667, 1329, 1157 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.57 (t, $J = 8.2$ Hz, 1H), 7.45 (t, $J = 8.1$ Hz, 2H), 7.27–7.10 (m, 7H), 5.73 (d, $J = 8.4$ Hz, 1H), 4.15–4.05 (m, 1H), 3.82–3.72 (m, 2H), 3.07 (d, $J = 7.7$ Hz, 1H), 2.80–2.72 (m, 1H), 2.57–2.48 (m, 1H), 2.37 (s, 3H), 1.82–1.73 (m, 2H), 1.42–1.23 (m, 2H), 1.11–0.91 (m, 2H), 0.61 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.9, 143.1, 141.5, 138.2, 137.8, 133.7, 129.4, 128.7, 128.3, 128.3, 128.2, 126.7, 125.7, 71.2, 54.4, 52.6, 37.6, 35.8, 32.1, 21.5, 19.2, 13.5. HRMS (ESI) calcd for $C_{28}H_{34}NO_4S$ $[M + H]^+$ 480.2209, found 480.2207.

***syn*,*anti*-4b:** Colorless oil. IR (neat) 3493, 3282, 1667, 1328, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70 (d, $J = 8.2$ Hz, 2H), 7.61–7.52 (m, 3H), 7.38 (t, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 5.72 (d, $J = 8.3$ Hz, 1H), 3.83–3.74 (m, 2H), 3.63–3.52 (m, 1H), 2.37 (s, 3H), 1.73–1.60 (m, 2H), 1.32–1.16 (m, 3H), 0.99 (d, $J = 6.6$ Hz, 3H), 0.84 (t, $J = 7.3$ Hz, 3H), 0.77 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.1, 142.7, 138.0, 136.3, 133.7, 129.2, 128.6, 128.2, 126.9, 77.3, 55.5, 47.4, 36.8, 33.2, 21.6, 19.8, 19.7, 19.4, 13.8. HRMS (ESI) calcd for $C_{23}H_{32}NO_4S$ $[M + H]^+$ 418.2052, found 418.2047.

***anti*,*anti*-4b:** Colorless oil. IR (neat) 3501, 3294, 1662, 1333, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.58 (t, $J = 8.2$ Hz, 1H), 7.46 (t, $J = 8.1$ Hz, 2H), 7.23 (d, $J = 7.7$ Hz, 2H), 5.81 (d, $J = 8.6$ Hz, 1H), 3.96 (t, $J = 5.4$ Hz, 1H), 3.76 (t, $J = 5.6$ Hz, 1H), 3.70–3.61 (m, 1H), 2.39 (s, 3H), 1.72–1.62 (m, 1H), 1.55–1.41 (m, 1H), 1.39–1.25 (m, 1H), 1.19–1.08 (m, 1H), 1.04–0.95 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.76 (d, $J = 6.8$ Hz, 3H), 0.64 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.5, 142.9, 138.3, 138.0, 133.5, 129.3, 128.6, 128.3, 126.7, 75.9, 54.2, 49.4, 36.0, 31.2, 21.5, 19.6, 19.2, 16.5, 13.5. HRMS (ESI) calcd for $C_{23}H_{32}NO_4S$ $[M + H]^+$ 418.2052, found 418.2061.

***anti*,*anti*-5a:** Colorless oil. IR (neat) 3500, 3306, 1663, 1327, 1157 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 8.2$ Hz, 1H), 7.41 (t, $J = 8.1$ Hz, 2H), 7.29–7.12 (m, 7H), 5.98 (d, $J = 8.7$ Hz, 1H), 4.12–4.00 (m, 1H), 3.79 (dd, $J = 6.6$, 4.6 Hz, 1H), 3.71 (dd, $J = 8.9$, 6.1 Hz, 1H), 2.82–2.52 (m, 1H), 2.60–2.50 (m, 1H), 2.48 (d, $J = 6.9$ Hz, 1H), 2.37 (s, 3H), 1.94–1.73 (m, 3H), 0.74 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.3, 142.7, 141.4, 138.8, 138.3, 133.4, 129.2, 128.5, 128.4, 128.3, 128.2, 126.6, 125.7, 72.1, 60.3, 50.2, 37.5, 31.9, 31.9, 21.5, 19.9, 18.8. HRMS (ESI) calcd for $C_{28}H_{34}NO_4S$ $[M + H]^+$ 480.2209, found 480.2209.

***anti*,*anti*-5b:** Colorless oil. IR (neat) 3518, 3306, 1665, 1330, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 8.2$ Hz, 1H), 7.43 (t, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 6.12 (d, $J = 8.7$ Hz,

1H), 3.93 (dd, $J = 7.6$, 4.5 Hz, 1H), 3.70–3.58 (m, 2H), 2.60–2.50 (m, 1H), 2.38 (s, 3H), 2.07 (d, $J = 6.4$ Hz, 1H), 1.85–1.69 (m, 2H), 0.93 (d, $J = 6.8$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.77 (d, $J = 6.8$ Hz, 3H), 0.72 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.0, 142.6, 139.0, 138.6, 133.3, 129.2, 128.5, 128.3, 126.5, 76.5, 59.9, 46.7, 32.2, 30.3, 21.5, 19.7, 19.5, 18.8, 15.5. HRMS (ESI) calcd for $C_{23}H_{32}NO_4S$ $[M + H]^+$ 418.2052, found 418.2079.

***anti*,*anti*-6a:** Colorless oil. IR (neat) 3517, 3286, 1664, 1325, 1155 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.2$ Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 8.2$ Hz, 1H), 7.45 (t, $J = 8.1$ Hz, 2H), 7.32–7.17 (m, 7H), 7.04 (d, $J = 8.1$ Hz, 1H), 4.18 (brs, 1H), 3.92 (d, $J = 8.1$ Hz, 1H), 3.65 (d, $J = 6.8$ Hz, 1H), 2.81–2.75 (m, 1H), 2.69–2.56 (m, 1H), 2.40 (s, 3H), 2.29 (d, $J = 5.1$ Hz, 1H), 2.25–2.10 (m, 1H), 1.98–1.78 (m, 1H), 0.71 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.0, 142.7, 141.7, 139.3, 138.8, 133.3, 129.3, 128.6, 128.5, 128.4, 128.4, 126.5, 125.8, 73.5, 64.2, 48.2, 37.7, 36.5, 31.9, 27.9, 21.5. HRMS (ESI) calcd for $C_{29}H_{36}NO_4S$ $[M + H]^+$ 494.2365, found 494.2330.

***anti*,*anti*-6b:** Colorless oil. IR (neat) 3532, 3284, 1665, 1327, 1156 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 8.2$ Hz, 1H), 7.45 (t, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 8.1$ Hz, 1H), 4.06 (dd, $J = 9.4$, 1.8 Hz, 1H), 3.92–3.86 (m, 1H), 3.58 (dd, $J = 8.2$, 1.8 Hz, 1H), 2.40 (s, 3H), 2.16–2.09 (m, 1H), 1.69 (d, $J = 5.1$ Hz, 1H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.87 (d, $J = 6.8$ Hz, 3H), 0.76 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 207.0, 142.5, 139.6, 139.1, 133.1, 129.3, 128.6, 128.5, 126.4, 76.9, 63.4, 44.9, 36.6, 29.3, 27.9, 21.5, 19.5, 14.0. HRMS (ESI) calcd for $C_{24}H_{34}NO_4S$ $[M + H]^+$ 432.2209, found 432.2229.

***syn*,*anti*-7a:** Colorless oil. IR (neat) 3467, 3251, 1665, 1321, 1157 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.2$ Hz, 2H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.44–7.33 (m, 4H), 7.19–7.05 (m, 8H), 7.00–6.93 (m, 4H), 6.50 (d, $J = 8.7$ Hz, 1H), 5.00 (dd, $J = 8.7$, 6.2 Hz, 1H), 4.05–3.80 (m, 2H), 3.69 (dd, $J = 6.1$, 1.8 Hz, 1H), 2.78–2.66 (m, 1H), 2.53–2.40 (m, 1H), 2.29 (s, 3H), 1.83–1.57 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.6, 142.7, 141.1, 138.9, 137.2, 136.4, 133.5, 129.0, 128.6, 128.4, 128.2, 128.2, 128.0, 127.5, 126.9, 126.6, 125.7, 70.3, 58.3, 54.1, 37.8, 32.6, 21.5. HRMS (ESI) calcd for $C_{31}H_{32}NO_4S$ $[M + H]^+$ 514.2052, found 514.2075.

***anti*,*anti*-7a:** Colorless oil. IR (neat) 3506, 3280, 1661, 1330, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.60 (d, $J = 8.2$ Hz, 2H), 7.45–7.36 (m, 3H), 7.29–6.91 (m, 14H), 6.38 (d, $J = 9.6$ Hz, 1H), 4.93 (dd, $J = 9.6$, 6.3 Hz, 1H), 3.87–3.80 (m, 2H), 2.82–2.69 (m, 2H), 2.58–2.45 (m, 1H), 2.27 (s, 3H), 1.96–1.65 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.8, 142.7, 141.2, 138.4, 138.3, 137.3, 133.4, 128.9, 128.3, 128.3, 128.2, 128.1, 127.2, 126.9, 126.4, 125.8, 71.6, 58.2, 55.6, 37.1, 32.0, 21.4. HRMS (ESI) calcd for $C_{31}H_{32}NO_4S$ $[M + H]^+$ 514.2052, found 514.2059.

Other Isomer-7a: Colorless oil. IR (neat) 3527, 3252, 1664, 1447, 1155 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.42–7.32 (m, 3H), 7.30–6.91 (m, 14H), 6.72 (d, $J = 9.6$ Hz, 1H), 5.11 (dd, $J = 9.9$, 3.6 Hz, 1H), 4.35–4.26 (m, 1H), 3.87 (dd, $J = 9.4$, 3.6 Hz, 1H), 3.69 (d, $J = 4.8$ Hz, 1H), 2.94–2.81 (m, 1H), 2.70–2.57 (m, 1H), 2.27 (s, 3H), 1.67–1.42 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.7, 143.0, 141.5, 138.4, 137.5, 136.8, 133.3, 129.0, 128.3, 128.1, 128.0, 127.8, 126.9, 126.8, 125.7, 125.6, 70.6, 57.8, 56.0, 37.0, 32.2, 21.4. HRMS (ESI) calcd for $C_{31}H_{32}NO_4S$ $[M + H]^+$ 514.2052, found 514.2047.

***syn*,*anti*-7b:** Colorless oil. IR (neat) 3474, 3226, 1669, 1319, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.47–7.37 (m, 4H), 7.26–7.15 (m, 5H), 6.95 (d, $J = 8.2$ Hz, 2H), 6.74 (d, $J = 8.9$ Hz, 1H), 5.04 (dd, $J = 8.9$, 4.8 Hz, 1H), 3.93 (d, $J = 10.7$ Hz, 1H), 3.82 (dd, $J = 4.8$, 1.8 Hz, 1H), 3.40–3.29 (m, 1H), 2.30 (s, 3H), 1.70–1.55 (m, 1H), 0.87 (d, $J = 6.8$ Hz, 3H), 0.60 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.9, 142.4, 138.9, 137.3, 135.8, 133.6, 128.9, 128.6, 128.4, 128.0, 127.3, 126.7, 126.3, 76.6, 58.5, 50.4, 33.1, 21.4, 19.5, 19.5. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1901.

***anti*,*anti*-7b:** Colorless oil. IR (neat) 3519, 3281, 1661, 1330, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.62 (d, $J = 7.6$ Hz, 2H), 7.44–7.35 (m, 3H), 7.25 (t, $J = 7.6$ Hz, 2H), 7.05–6.92 (m, 7H), 6.53 (d, $J = 9.2$ Hz, 1H), 4.88 (dd, $J = 9.2$, 6.5 Hz, 1H), 3.99 (t, $J = 6.5$ Hz, 1H), 3.60–3.53 (m, 1H), 2.67 (brs, 1H), 2.29 (s, 3H), 1.81–1.70 (m, 1H), 0.92 (d, $J = 6.8$ Hz, 3H), 0.79 (d, $J = 6.8$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.3, 142.6, 138.7, 138.4, 137.4, 133.2, 128.9, 128.2, 128.2, 128.1, 127.2, 126.8, 126.3, 76.5, 58.1, 52.8, 30.6, 21.4, 19.6, 16.4. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1904.

Other Isomer-7b: Colorless oil. IR (neat) 3486, 3290, 1660, 1319, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.43–7.32 (m, 3H), 7.26–7.17 (m, 3H), 7.04–6.92 (m, 6H), 6.72 (d, $J = 9.6$ Hz, 1H), 5.08 (dd, $J = 9.2$, 3.1 Hz, 1H), 4.12–4.06 (m, 1H), 3.91 (dd, $J = 9.6$, 3.5 Hz, 1H), 3.23 (d, $J = 3.9$ Hz, 1H), 2.26 (s, 3H), 1.43–1.27 (m, 1H), 0.96 (d, $J = 6.8$ Hz, 1H), 0.74 (d, $J = 6.8$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.1, 142.9, 138.7, 137.4, 136.9, 133.2, 129.0, 128.2, 128.0, 127.7, 126.9, 126.8, 125.8, 74.8, 56.1, 55.3, 30.7, 21.3, 20.7, 14.8. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1885.

***anti*-8a:** Colorless oil. IR (neat) 3503, 3283, 1671, 1328, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.47 (t, $J = 8.2$ Hz, 2H), 7.26–7.10 (m, 5H), 7.08 (d, $J = 7.2$ Hz, 2H), 5.12 (t, $J = 6.3$ Hz, 1H), 4.00–3.84 (m, 2H), 3.42–3.27 (m, 2H), 2.96 (d, $J = 8.9$ Hz, 1H), 2.86–2.73 (m, 1H), 2.64–2.51 (m, 1H), 2.40 (s, 3H), 1.75–1.58 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.5, 143.3, 141.2, 136.6, 136.5, 133.9, 129.6, 128.7, 128.4, 128.2, 128.2, 126.8, 125.7, 71.0, 50.6, 42.5, 36.9, 32.3, 21.5. HRMS (ESI) calcd for $C_{25}H_{28}NO_4S$ $[M + H]^+$ 438.1739, found 438.1755.

***anti*-8b:** Colorless oil. IR (neat) 3508, 3282, 1667, 1330, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 5.59–5.47 (m, 1H), 4.05–3.97 (m, 1H), 3.56–3.46 (m, 1H), 3.37–3.06 (m, 3H), 2.40 (s, 3H), 1.67–1.56 (m, 1H), 0.96 (d, $J = 6.4$ Hz, 3H), 0.77 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.5, 143.3, 136.8, 136.6, 133.9, 129.6, 128.8, 128.4, 126.8, 77.2, 47.4, 43.3, 32.4, 21.5, 19.5, 18.7. HRMS (ESI) calcd for $C_{20}H_{26}NO_4S$ $[M + H]^+$ 376.1583, found 376.1608.

***syn*,*anti*-9a:** Colorless oil. IR (neat) 3483, 3278, 1701, 1328, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.30–7.15 (m, 5H), 7.10–6.93 (m, 7H), 6.37 (d, $J = 9.2$ Hz, 1H), 5.35 (d, $J = 5.0$ Hz, 1H), 4.90 (t, $J = 9.6$ Hz, 1H), 4.06 (d, $J = 7.6$ Hz, 1H), 3.37 (dd, $J = 9.9$, 2.8 Hz, 1H), 2.31 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 209.3, 143.3, 141.4, 138.2, 136.8, 129.2, 128.4, 128.2, 127.6, 127.1, 127.1, 126.8, 125.1, 70.8, 64.0, 56.9, 32.8, 21.5. HRMS (ESI)

calcd for $C_{24}H_{26}NO_4S$ $[M + H]^+$ 424.1583, found 424.1603.

***anti*,*anti*-9a:** Colorless oil. IR (neat) 3492, 3282, 1706, 1328, 1157 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.50–7.31 (m, 7H), 7.10–6.93 (m, 5H), 6.78 (d, $J = 7.6$ Hz, 2H), 6.51 (d, $J = 9.5$ Hz, 1H), 4.93 (d, $J = 8.1$ Hz, 1H), 4.39 (dd, $J = 9.2$, 5.1 Hz, 1H), 3.24 (dd, $J = 8.1$, 5.1 Hz, 1H), 2.70 (brs, 1H), 2.28 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.6, 142.6, 141.0, 138.1, 137.8, 128.9, 128.7, 128.4, 128.3, 127.2, 126.7, 126.3, 126.1, 74.1, 63.4, 57.3, 35.1, 21.4. HRMS (ESI) calcd for $C_{24}H_{26}NO_4S$ $[M + H]^+$ 424.1583, found 424.1606.

***syn*,*anti*-9b:** Colorless oil. IR (neat) 3506, 3270, 1702, 1307, 1158 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.26–7.04 (m, 10H), 6.91 (d, $J = 8.2$ Hz, 2H), 6.02 (d, $J = 9.2$ Hz, 1H), 4.93 (t, $J = 8.1$ Hz, 1H), 3.92–3.86 (m, 1H), 3.52 (d, $J = 9.1$ Hz, 1H), 2.85–2.70 (m, 2H), 2.57–2.44 (m, 1H), 2.33 (s, 3H), 1.99 (s, 3H), 1.91–1.75 (m, 1H), 1.71–1.56 (m, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 209.3, 143.2, 141.2, 137.9, 137.1, 129.2, 128.5, 128.3, 128.2, 127.7, 127.0, 126.5, 125.8, 69.2, 61.2, 57.4, 37.4, 32.6, 30.8, 21.5. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1898.

***anti*,*anti*-9b:** Colorless oil. IR (neat) 3503, 3250, 1687, 1327, 1156 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.42 (d, $J = 8.2$ Hz, 2H), 7.30–6.88 (m, 12H), 6.35 (d, $J = 9.9$ Hz, 1H), 4.76 (dd, $J = 9.7$, 6.8 Hz, 1H), 3.78–3.53 (m, 1H), 2.98 (t, $J = 6.8$ Hz, 1H), 2.80–2.71 (m, 1H), 2.63–2.52 (m, 1H), 2.45 (d, $J = 6.8$ Hz, 1H), 2.27 (s, 3H), 2.04 (s, 3H), 2.05–1.86 (m, 1H), 1.78–1.69 (m, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.7, 142.8, 141.1, 138.0, 137.3, 129.0, 128.4, 128.3, 128.3, 127.3, 126.8, 126.2, 125.9, 71.0, 62.0, 57.3, 36.8, 34.4, 31.8, 21.4. HRMS (ESI) calcd for $C_{26}H_{30}NO_4S$ $[M + H]^+$ 452.1896, found 452.1908.

***syn*,*anti*-9c:** Colorless oil. IR (neat) 3472, 3242, 1709, 1306, 1154 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.14–6.94 (m, 7H), 6.14 (d, $J = 9.4$ Hz, 1H), 5.00 (dd, $J = 9.0$, 7.4 Hz, 1H), 3.46 (d, $J = 9.6$ Hz, 1H), 3.29 (t, $J = 9.4$ Hz, 1H), 3.01 (d, $J = 7.1$ Hz, 1H), 2.33 (s, 3H), 2.07 (s, 3H), 1.73–1.58 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.69 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 209.9, 143.0, 138.0, 137.3, 129.2, 128.4, 127.5, 126.9, 126.5, 75.6, 58.5, 57.5, 32.7, 30.8, 21.5, 19.8, 19.5. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_4S$ $[M + Na]^+$ 412.1559, found 412.1547.

***anti*,*anti*-9c:** Colorless oil. IR (neat) 3512, 3272, 1698, 1329, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.43 (d, $J = 8.2$ Hz, 2H), 7.09–6.92 (m, 7H), 6.43 (d, $J = 9.6$ Hz, 1H), 4.71 (dd, $J = 9.6$, 6.4 Hz, 1H), 3.50–3.42 (m, 1H), 3.12 (t, $J = 6.6$ Hz, 1H), 2.35 (d, $J = 6.4$ Hz, 1H), 2.29 (s, 3H), 1.96 (s, 3H), 1.82–1.71 (m, 1H), 0.91 (d, $J = 6.8$ Hz, 3H), 0.87 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 214.2, 142.7, 138.4, 137.5, 128.9, 128.3, 127.2, 126.8, 126.1, 75.7, 59.1, 57.2, 34.5, 30.2, 21.4, 19.5, 16.0. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_4S$ $[M + Na]^+$ 412.1559, found 412.1562.

***trans*-2-Benzoyl-1-mesyl-3-methylaziridine (10).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (190 mg, 1.18 mmol) and DMAP (288 mg, 2.36 mmol) in CH_2Cl_2 (4 mL) was added mesyl chloride (MsCl) (203 mg, 1.77 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-1-mesyl-3-methylaziridine (**10**) (140 mg, 85%). Colorless oil. IR (neat) 1691, 1319, 1155 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 4.13 (d, $J = 4.1$ Hz, 1H), 3.25 (dq, $J = 4.1$, 5.9 Hz, 1H), 3.13 (s, 3H), 1.80 (d, $J = 5.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.2, 135.3, 134.1, 128.8, 128.3, 47.2, 45.1, 42.5, 13.9. HRMS (ESI) calcd for $C_{11}H_{14}NO_3S$ $[M + H]^+$ 240.0694, found 240.0705.

***trans*-2-Benzoyl-3-methyl-1-(2,4,6-trimethylbenzenesulfonyl)-aziridine (11).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (250 mg, 1.55 mmol) and Et_3N (470 mg, 4.65 mmol) in CH_2Cl_2 (3 mL) was added 2,4,6-trimethylbenzenesulfonyl chloride (MtsCl) (508 mg, 2.33 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-3-methyl-1-(2,4,6-trimethylbenzenesulfonyl)aziridine (**11**) (335 mg, 63%). Colorless oil. IR (neat) 1690, 1324, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 6.91 (s, 2H), 4.13 (d, $J = 4.0$ Hz, 1H), 3.24 (dq, $J = 4.0$, 5.9 Hz, 1H), 2.65 (s, 6H), 2.26 (s, 3H), 1.80 (d, $J = 5.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.8, 142.8, 139.6, 135.5, 134.0, 133.8, 131.7, 128.6, 128.3, 46.8, 45.1, 23.0, 21.0, 14.1. HRMS (ESI) calcd for $C_{19}H_{22}NO_3S$ $[M + H]^+$ 344.1320, found 344.1317.

***trans*-1-Acetyl-2-benzoyl-3-methylaziridine (12).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (184 mg, 1.14 mmol) and Et_3N (346 mg, 3.42 mmol) in CH_2Cl_2 (3 mL) was added Ac_2O (174 mg, 1.71 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-1-acetyl-2-benzoyl-3-methylaziridine (**12**) (230 mg, 99%). Colorless oil. IR (neat) 1701, 1231 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 3.87 (d, $J = 2.5$ Hz, 1H), 3.24 (dq, $J = 2.5$, 5.6 Hz, 1H), 2.15 (s, 3H), 1.48 (d, $J = 5.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.1, 180.2, 136.0, 133.8, 128.7, 128.3, 44.8, 41.8, 24.5, 17.3. HRMS (ESI) calcd for $C_{12}H_{13}NNaO_2$ $[M + Na]^+$ 226.0844, found 226.0826.

***trans*-1,2-Dibenzoyl-3-methylaziridine (13).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (232 mg, 1.44 mmol) and Et_3N (437 mg, 4.32 mmol) in CH_2Cl_2 (5 mL) was added benzoyl chloride (303 mg, 2.16 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-1,2-dibenzoyl-3-methylaziridine (**13**) (332 mg, 87%). Colorless oil. IR (neat) 1686, 1672, 1228 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 8.04 (d, $J = 8.0$ Hz, 2H), 8.01 (d, $J = 7.6$ Hz, 2H), 7.62–7.37 (m, 6H), 4.05 (d, $J = 2.6$ Hz, 1H), 3.20 (dq, $J = 2.6$, 5.6 Hz, 1H), 1.44 (d, $J = 5.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.1, 176.5, 136.1, 133.6, 132.4, 128.6, 128.4, 128.3, 128.3, 45.1, 42.3, 16.8. HRMS (ESI) calcd for $C_{17}H_{16}NO_2$ [M +

H]$^+$ 266.1181, found 266.1173.

***trans*-2-Benzoyl-1-(1,1-dimethylethoxycarbonyl)-3-methylaziridine (14).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (300 mg, 1.86 mmol) and DMAP (454 mg, 3.72 mmol) in CH_3CN (5 mL) was added Boc_2O (487 mg, 2.23 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-1-(1,1-dimethylethoxycarbonyl)-3-methylaziridine (**14**) (312 mg, 64%). Colorless oil. IR (neat) 1726, 1680, 1159 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.0$ Hz, 2H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 3.71 (d, $J = 2.6$ Hz, 1H), 2.96 (dq, $J = 2.6$, 5.4 Hz, 1H), 1.43 (s, 9H), 1.41 (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.2, 159.2, 136.5, 133.4, 128.5, 128.1, 81.3, 44.2, 41.2, 27.8, 16.7. HRMS (ESI) calcd for $C_{15}H_{20}NO_3$ $[M + H]^+$ 262.1443, found 262.1458.

***trans*-2-Benzoyl-1-(benzyloxycarbonyl)-3-methylaziridine (15).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (256 mg, 1.59 mmol) and Na_2CO_3 (253 mg, 2.39 mmol) in THF–H_2O (6 mL, 1:1) was added CbzCl (325 mg, 1.91 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-1-(benzyloxycarbonyl)-3-methylaziridine (**15**) (446 mg, 95%). Colorless oil. IR (neat) 1729, 1677, 1302, 1197 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.37–7.08 (m, 5H), 5.14 (d, $J = 12.2$ Hz, 1H), 5.06 (d, $J = 12.2$ Hz, 1H), 3.72 (d, $J = 2.0$ Hz, 1H), 2.90 (dq, $J = 2.0$, 5.4 Hz, 1H), 1.35 (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.0, 160.6, 136.2, 135.4, 133.6, 128.6, 128.4, 128.2, 128.2, 128.0, 68.2, 44.4, 42.0, 16.9. HRMS (ESI) calcd for $C_{18}H_{18}NO_3$ $[M + H]^+$ 296.1287, found 296.1311.

***trans*-2-Benzoyl-1-(9-fluorenylmethoxycarbonyl)-3-methylaziridine (16).** To a solution of 2-benzoyl-3-methyl-1*H*-aziridine (180 mg, 1.12 mmol) and Na_2CO_3 (178 mg, 1.68 mmol) in THF–H_2O (4 mL, 1:1) was added FmocCl (348 mg, 1.34 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford *trans*-2-benzoyl-1-(9-fluorenylmethoxycarbonyl)-3-methylaziridine (**16**) (421 mg, 98%). Colorless oil. IR (neat) 1727, 1677, 1303, 1202 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.0$ Hz, 2H), 7.74–7.45 (m, 7H), 7.38–7.30 (m, 2H), 7.26–7.14 (m, 2H), 4.56 (dd, $J = 10.5$, 6.8 Hz, 1H), 4.40 (dd, $J = 10.5$, 6.9 Hz, 1H), 4.23 (t, $J = 6.9$ Hz, 1H), 3.78 (d, $J = 2.8$ Hz, 1H), 2.97 (dq, $J = 2.8$, 5.4 Hz, 1H), 1.39 (d, $J = 5.4$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.0, 160.6, 143.6, 143.5, 141.1, 136.2, 133.8, 128.7, 128.3, 127.5, 126.9, 125.1, 124.9, 119.8, 68.2, 46.9, 44.4, 42.2, 16.9. HRMS (ESI) calcd for $C_{25}H_{22}NO_3$ $[M + H]^+$ 384.1600, found 384.1632.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of Aziridinyl Ketone with Aldehyde. (Table 4, Entry 1). To a mixture of *trans*-2-benzoyl-3-methyl-1-mesylaziridine (**10**) (42.1 mg, 0.176 mmol) and 3-phenylpropanal (23.6 mg, 0.194 mmol) in THF (4 mL) at −78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 4.4 mL, 0.44 mmol). After the reaction mixture was stirred for 1 h at −78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford *syn*,*anti*-**10a** (18.3 mg, 28%) and *anti*,*anti*-**10a** (44.9 mg, 68%), respectively.

***syn*,*anti*-10a:** Colorless oil. IR (neat) 3495, 3278, 1666, 1322, 1135 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.63 (t, $J = 8.2$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 2H), 7.25–7.05 (m, 5H), 5.08 (d, $J = 9.2$ Hz, 1H), 4.13–4.02 (m, 2H), 3.57 (d, $J = 10.2$ Hz, 1H), 3.53 (dd, $J = 7.6$, 2.4 Hz, 1H), 2.90 (s, 3H), 2.87–2.77 (m, 1H), 2.72–2.58 (m, 1H), 1.78–1.60 (m, 2H), 1.30 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.7, 141.2, 137.0, 134.2, 129.0, 128.9, 128.4, 128.3, 125.9, 70.0, 54.0, 50.6, 41.6, 38.0, 32.5, 22.2. HRMS (ESI) calcd for $C_{20}H_{26}NO_4S$ $[M + H]^+$ 376.1583, found 376.1595.

***anti*,*anti*-10a:** Colorless oil. IR (neat) 3466, 3291, 1651, 1319, 1162 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.27–7.09 (m, 5H), 5.20 (d, $J = 9.7$ Hz, 1H), 4.09–3.97 (m, 2H), 3.66 (dd, $J = 6.8$, 5.4 Hz, 1H), 2.88 (d, $J = 8.1$ Hz, 1H), 2.85–2.77 (m, 1H), 2.79 (s, 3H), 2.72–2.59 (m, 1H), 1.86–1.66 (m, 2H), 1.31 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.4, 141.2, 138.0, 134.0, 128.9, 128.4, 128.3, 128.3, 125.9, 71.2, 54.6, 50.7, 41.6, 37.7, 32.2, 21.5. HRMS (ESI) calcd for $C_{20}H_{26}NO_4S$ $[M + H]^+$ 376.1583, found 376.1613.

***syn*,*anti*-11a:** Colorless oil. IR (neat) 3493, 3291, 1668, 1324, 1157 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.63 (d, $J = 8.2$ Hz, 2H), 7.53 (t, $J = 8.2$ Hz, 1H), 7.36 (t, $J = 7.9$ Hz, 2H), 7.25–7.05 (m, 5H), 6.80 (s, 2H), 5.57 (d, $J = 9.1$ Hz, 1H), 4.13–4.05 (m, 1H), 3.95–3.83 (m, 1H), 3.71 (brd, $J = 8.6$ Hz, 1H), 3.44 (dd, $J = 5.9$, 2.6 Hz, 1H), 2.87–2.75 (m, 1H), 2.66–2.53 (m, 1H), 2.48 (s, 6H), 2.25 (s, 3H), 1.82–1.75 (m, 1H), 1.68–1.60 (m, 1H), 1.17 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.5, 141.7, 141.3, 138.5, 136.5, 134.6, 133.6, 131.8, 128.6, 128.3, 128.3, 128.1, 125.8, 70.3, 53.8, 50.7, 37.9, 32.6, 23.0, 21.1, 21.0. HRMS (ESI) calcd for $C_{28}H_{33}KNO_4S$ $[M + K]^+$ 518.1767, found 518.1764.

***anti*,*anti*-11a:** Colorless oil. IR (neat) 3493, 3341, 1660, 1328, 1156 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.2$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 2H), 7.27–7.07 (m, 5H), 6.89 (s, 2H), 5.69 (d, $J = 9.4$ Hz, 1H), 4.10–3.99 (m, 1H), 3.89–3.79 (m, 1H), 3.63 (t, $J = 5.6$ Hz, 1H), 2.82–2.69 (m, 1H), 2.59 (s, 6H), 2.58–2.44 (m, 1H), 2.26 (s, 3H), 1.77–1.64 (m, 2H), 1.05 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.9, 141.8, 141.3, 138.4, 137.9, 135.1, 133.7, 131.8, 128.7, 128.4, 128.3, 128.2, 125.8, 71.5, 54.6, 50.1, 37.2, 31.9, 23.0, 21.0, 20.5. HRMS (ESI) calcd for $C_{28}H_{33}KNO_4S$ $[M + K]^+$ 518.1767, found 518.1764.

***syn*,*anti*-12a:** Colorless oil. IR (neat) 3302, 1667, 1373, 1213 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.49–7.09 (m, 7H), 6.22 (d, $J = 8.3$ Hz, 1H), 4.51–4.40 (m, 1H), 4.08–3.90 (m, 2H), 3.61 (dd, $J = 6.1$, 2.1 Hz, 1H), 2.84–2.77 (m, 1H), 2.73–2.64 (m, 1H), 1.89 (s, 3H), 1.85–1.69 (m, 2H), 1.26 (d, $J = 6.6$ Hz, 3H).

^{13}C NMR (68 MHz, $CDCl_3$) δ 203.3, 169.8, 141.3, 137.3, 133.6, 128.7, 128.3, 128.2, 128.1, 125.7, 70.1, 53.1, 46.5, 37.8, 32.4, 23.3, 19.3. HRMS (ESI) calcd for $C_{21}H_{25}KNO_3$ $[M + K]^+$ 378.1472, found 378.1460.

***anti*,*anti*-12a:** Colorless oil. IR (neat) 3400, 3311, 1658, 1374 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 7.28–7.11 (m, 5H), 6.49 (d, $J = 8.6$ Hz, 1H), 4.46–4.41 (m, 1H), 4.00–3.80 (m, 1H), 3.84 (dd, $J = 7.2$, 4.5 Hz, 1H), 2.90–2.77 (m, 1H), 2.72–2.62 (m, 1H), 2.63 (d, $J = 7.3$ Hz, 1H), 2.00–1.67 (m, 2H), 1.91 (s, 3H), 1.12 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.9, 169.4, 141.1, 138.2, 133.7, 128.7, 128.4, 128.3, 128.3, 125.8, 71.2, 53.7, 45.2, 36.6, 31.6, 23.5, 19.7. HRMS (ESI) calcd for $C_{21}H_{26}NO_3$ $[M + H]^+$ 340.1913, found 340.1900.

***syn*,*anti*-13a:** Colorless oil. IR (neat) 3326, 1663, 1542 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 7.4$ Hz, 2H), 7.63–7.38 (m, 7H), 7.29–7.02 (m, 4H), 4.74–4.65 (m, 1H), 4.23–4.10 (m, 2H), 3.71 (dd, $J = 5.6$, 2.1 Hz, 1H), 2.90–2.80 (m, 1H), 2.73–2.65 (m, 1H), 1.96–1.65 (m, 2H), 1.40 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.7, 166.9, 141.3, 137.1, 134.1, 133.8, 131.4, 128.9, 128.4, 128.3, 128.3, 128.3, 126.8, 125.8, 70.5, 52.8, 47.1, 38.2, 32.6, 19.6. HRMS (ESI) calcd for $C_{26}H_{28}NO_3$ $[M + H]^+$ 402.2069, found 402.2068.

***anti*,*anti*-13a:** Colorless oil. IR (neat) 3480, 3354, 1650, 1524 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 7.4$ Hz, 2H), 7.63–7.25 (m, 7H), 7.09–7.02 (m, 4H), 4.69–4.62 (m, 1H), 4.10–3.98 (m, 1H), 3.93 (dd, $J = 7.6$, 4.1 Hz, 1H), 2.83–2.76 (m, 1H), 2.70–2.62 (m, 2H), 2.05–1.82 (m, 2H), 1.21 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.2, 166.5, 140.9, 138.3, 134.1, 133.7, 131.4, 128.8, 128.5, 128.4, 128.3, 128.2, 126.8, 125.7, 71.5, 54.0, 45.5, 36.4, 31.5, 19.9. HRMS (ESI) calcd for $C_{26}H_{28}NO_3$ $[M + H]^+$ 402.2069, found 402.2056.

***anti*,*anti*-14a:** Colorless oil. IR (neat) 3508, 3385, 1688, 1521 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.26–7.07 (m, 5H), 5.29 (d, $J = 8.7$ Hz, 1H), 4.17–3.98 (m, 2H), 3.88 (t, $J = 8.0$ Hz, 1H), 2.90–2.77 (m, 1H), 2.88 (d, $J = 8.1$ Hz, 1H), 2.71–2.58 (m, 1H), 1.95–1.72 (m, 2H), 1.38 (s, 9H), 1.19 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.6, 155.1, 141.4, 138.2, 133.6, 128.7, 128.4, 128.3, 128.3, 125.7, 71.5, 53.9, 46.9, 37.3, 32.4, 32.2, 28.4, 19.7. HRMS (ESI) calcd for $C_{24}H_{31}KNO_4$ $[M + K]^+$ 436.1890, found 436.1867.

***anti*,*anti*-15a:** Colorless oil. IR (neat) 3411, 1700, 1507, 1238 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47–7.06 (m, 12H), 5.63 (d, $J = 8.8$ Hz, 1H), 5.04 (s, 2H), 4.34–4.13 (m, 1H), 4.10–3.98 (m, 1H), 3.85 (t, $J = 5.8$ Hz, 1H), 2.88–2.75 (m, 2H), 2.68–2.55 (m, 1H), 1.90–1.68 (m, 2H), 1.17 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.6, 155.6, 141.5, 138.1, 133.6, 128.7, 128.4, 128.3, 128.2, 128.0, 127.8, 125.7, 71.4, 66.6, 53.7, 47.4, 37.2, 32.0, 19.7. HRMS (ESI) calcd for $C_{27}H_{30}NO_4$ $[M + H]^+$ 432.2175, found 432.2214.

***anti*,*anti*-16a:** Colorless oil. IR (neat) 3412, 3335, 1687, 1536, 1448, 1257 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.00 (d, $J = 8.2$ Hz, 2H), 7.76–7.00 (m, 16H), 5.64 (d, $J = 8.4$ Hz, 1H), 4.38–4.00 (m, 5H), 3.87 (t, $J = 5.6$ Hz, 1H), 2.84–2.75 (m, 2H), 2.72–2.57 (m, 1H), 1.90–1.58 (m, 2H), 1.21 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.7, 155.6, 143.8, 141.3, 141.2, 138.1, 133.7, 128.7, 128.4, 128.3, 128.3, 127.6, 126.9, 125.8, 125.0, 119.9, 71.4, 66.8, 53.7, 47.5, 47.2, 37.3, 32.0, 19.7. HRMS (ESI) calcd for $C_{34}H_{34}NO_4$ $[M + H]^+$ 520.2488, found 520.2504.

***trans*-2-Benzoyl-1-(9-fluorenylmethoxycarbonyl)-3-propylaziridine (17).** Fmoc-aziridines were prepared by the same procedure for **16**. Colorless oil. IR (neat) 1732, 1672, 1305, 1201 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.71–7.42 (m, 7H), 7.36–7.27 (m, 2H), 7.26–7.11 (m, 2H), 4.54 (dd, $J = 10.6$, 6.8 Hz, 1H), 4.41 (dd, $J = 10.8$, 6.9 Hz, 1H), 4.23 (t, $J = 6.9$ Hz, 1H), 3.83 (d, $J = 2.6$ Hz, 1H), 2.91–2.85 (m, 1H), 1.62–1.49 (m, 4H), 0.97 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.0, 160.6, 143.6, 143.5, 141.0, 136.1, 133.7, 128.6, 128.2, 127.4, 126.8, 126.7, 125.0, 124.8, 119.7, 68.1, 46.9, 46.7, 43.4, 33.5, 20.1, 13.7. HRMS (ESI) calcd for $C_{27}H_{25}NNaO_3$ $[M + Na]^+$ 434.1732, found 434.1710.

***trans*-2-Benzoyl-1-(9-fluorenylmethoxycarbonyl)-3-isopropylaziridine (18).** Colorless oil. IR (neat) 1727, 1203 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.71–7.42 (m, 7H), 7.35–7.27 (m, 2H), 7.22–7.11 (m, 2H), 4.53 (dd, $J = 10.6$, 6.9 Hz, 1H), 4.42 (dd, $J = 10.3$, 7.0 Hz, 1H), 4.24 (t, $J = 6.9$ Hz, 1H), 3.92 (d, $J = 2.6$ Hz, 1H), 2.73 (dd, $J = 7.3$, 2.6 Hz, 1H), 1.74–1.58 (m, 1H), 1.09 (d, $J = 6.8$ Hz, 3H), 1.01 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 192.9, 160.6, 143.7, 143.5, 141.0, 136.1, 133.7, 128.6, 128.1, 127.4, 127.4, 126.8, 126.8, 125.0, 124.8, 119.6, 68.2, 52.9, 46.8, 42.3, 30.5, 19.6, 19.2. HRMS (ESI) calcd for $C_{27}H_{25}NNaO_3$ $[M + Na]^+$ 434.1732, found 434.1741.

***trans*-2-Benzoyl-1-(9-fluorenylmethoxycarbonyl)-3-phenylaziridine (19).** Colorless oil. IR (neat) 1732, 1677, 1217 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.67–7.07 (m, 16H), 4.55 (dd, $J = 10.4$, 7.1 Hz, 1H), 4.41 (dd, $J = 10.4$, 7.4 Hz, 1H), 4.25 (t, $J = 7.1$ Hz, 1H), 4.11 (d, $J = 2.5$ Hz, 1H), 3.96 (d, $J = 2.5$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.7, 160.1, 143.6, 143.4, 141.0, 136.0, 135.4, 133.9, 128.7, 128.5, 128.4, 128.3, 127.5, 127.4, 126.8, 126.8, 126.3, 125.1, 125.0, 119.7, 68.6, 47.6, 47.1, 46.8. HRMS (ESI) calcd for $C_{30}H_{23}NNaO_3$ $[M + Na]^+$ 468.1576, found 468.1605.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of Aziridinyl Ketone with Aldehyde. (Table 5, Entry 1). To a mixture of *trans*-2-benzoyl-1-(9-fluorenylmethoxycarbonyl)-3-methylaziridine (**16**) (57.5 mg, 0.150 mmol) and 3-phenylpropanal (22.1 mg, 0.165 mmol) in THF (4 mL) at -78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 3.8 mL, 0.38 mmol). After the reaction mixture was stirred for 1 h at -78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford *anti*,*anti*-**16a** (73.2 mg, 94%).

***anti*,*anti*-16b:** Colorless oil. IR (neat) 3403, 1702, 1505, 1478, 1241 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.2$ Hz, 2H), 7.79–7.10 (m, 16H), 5.97 (d, $J = 8.7$ Hz, 1H), 5.20–5.11 (m, 1H), 4.49–4.28 (m, 3H), 4.23–4.11 (m, 1H), 3.78–3.67 (m, 1H), 2.63 (d, $J = 1.8$ Hz, 1H), 1.10 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.1, 155.3, 143.8, 141.2, 138.5, 133.3, 128.6, 128.5, 128.3, 128.1, 127.6, 127.0, 126.2, 125.6, 125.0, 119.0, 74.7, 66.6, 60.0, 55.8, 47.3, 21.1. HRMS (ESI) calcd for $C_{32}H_{30}NO_4$ $[M + H]^+$ 492.2175, found 492.2209.

***anti*,*anti*-16c:** Colorless oil. IR (neat) 3407, 1705, 1505, 1448, 1244 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.03 (d, $J = 8.2$ Hz, 2H), 7.77–7.22 (m, 11H), 5.80 (d, $J = 8.6$ Hz, 1H), 4.41–4.05 (m, 4H), 3.96 (t, $J = 5.4$ Hz, 1H), 3.90–3.80 (m, 1H), 2.71 (d, $J =$

7.1 Hz, 1H), 1.85–1.75 (m, 1H), 1.21 (d, $J = 6.4$ Hz, 3H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.2, 155.6, 143.8, 141.1, 138.3, 133.6, 128.7, 128.4, 127.6, 126.9, 125.9, 119.8, 76.7, 66.7, 50.5, 47.4, 47.2, 31.2, 19.9, 19.7, 16.3. HRMS (ESI) calcd for $C_{29}H_{32}NO_4$ $[M + H]^+$ 458.2331, found 458.2338.

***syn*,*anti*-17a:** Colorless oil. IR (neat) 3358, 1686, 1534, 1449, 1226 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.78–7.06 (m, 16H), 5.40 (d, $J = 9.1$ Hz, 1H), 4.43–4.25 (m, 2H), 4.19–3.95 (m, 3H), 3.88 (d, $J = 6.5$ Hz, 1H), 3.75 (dd, $J = 6.8$, 2.1 Hz, 1H), 2.86–2.80 (m, 1H), 2.78–2.55 (m, 1H), 1.92–1.60 (m, 2H), 1.50–1.20 (m, 4H), 0.86 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.0, 156.0, 143.9, 141.4, 141.2, 137.4, 133.7, 128.8, 128.3, 128.2, 127.6, 126.9, 125.8, 125.0, 125.0, 119.8, 70.5, 66.6, 52.2, 52.1, 47.3, 38.1, 35.6, 32.6, 19.8, 13.8. HRMS (ESI) calcd for $C_{36}H_{38}NO_4$ $[M + H]^+$ 548.2801, found 548.2819.

***anti*,*anti*-17a:** Colorless oil. IR (neat) 3354, 1686, 1530, 1449, 1260 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.2$ Hz, 2H), 7.77–7.06 (m, 16H), 5.67 (d, $J = 9.4$ Hz, 1H), 4.41–4.25 (m, 2H), 4.18–4.05 (m, 3H), 3.87 (t, $J = 5.9$ Hz, 1H), 2.83–2.78 (m, 1H), 2.77–2.60 (m, 2H), 2.08–1.71 (m, 2H), 1.65–1.15 (m, 4H), 0.81 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.7, 156.0, 143.8, 141.2, 141.1, 138.3, 133.6, 128.7, 128.4, 128.3, 127.5, 126.9, 125.8, 125.0, 125.0, 119.0, 71.6, 66.7, 53.2, 51.4, 47.3, 37.1, 36.1, 31.9, 19.6, 13.8. HRMS (ESI) calcd for $C_{36}H_{38}NO_4$ $[M + H]^+$ 548.2801, found 548.2801.

***anti*,*anti*-17b:** Colorless oil. IR (neat) 3411, 1709, 1668, 1507, 1241 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, $J = 8.2$ Hz, 2H), 7.77–7.22 (m, 11H), 5.81 (d, $J = 8.6$ Hz, 1H), 4.38–4.26 (m, 2H), 4.18 (t, $J = 6.9$ Hz, 1H), 4.09–3.93 (m, 2H), 3.90–3.82 (m, 1H), 2.41 (d, $J = 6.6$ Hz, 1H), 1.91–1.84 (m, 1H), 1.55–1.20 (m, 4H), 0.97 (d, $J = 6.8$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 3H), 0.81 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.3, 156.0, 143.8, 141.1, 138.6, 133.5, 128.6, 128.4, 127.5, 126.9, 124.9, 119.0, 76.8, 66.6, 51.4, 49.9, 47.3, 36.2, 30.8, 19.8, 19.6, 15.8, 13.8. HRMS (ESI) calcd for $C_{31}H_{36}NO_4$ $[M + H]^+$ 486.2644, found 486.2647.

***syn*,*anti*-18a:** Colorless oil. IR (neat) 3343, 1687, 1535, 1248 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.61–7.08 (m, 14H), 5.55 (d, $J = 10.2$ Hz, 1H), 4.37–4.25 (m, 2H), 4.17 (t, $J = 6.9$ Hz, 1H), 4.11–3.97 (m, 3H), 3.67 (d, $J = 5.9$ Hz, 1H), 2.86–2.78 (m, 1H), 2.71–2.61 (m, 1H), 1.90–1.75 (m, 2H), 1.68–1.57 (m, 1H), 0.96 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.2, 156.3, 143.9, 143.6, 141.2, 141.1, 136.8, 133.5, 128.7, 128.2, 128.0, 127.4, 126.8, 125.7, 124.9, 124.9, 119.7, 70.2, 66.6, 57.3, 49.9, 47.2, 38.2, 32.5, 31.0, 20.2, 18.5. HRMS (ESI) calcd for $C_{36}H_{38}NO_4$ $[M + H]^+$ 548.2801, found 548.2807.

***anti*,*anti*-18a:** Colorless oil. IR (neat) 3411, 1718, 1666, 1506, 1235 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 7.3$ Hz, 2H), 7.78–7.05 (m, 16H), 5.94 (d, $J = 10.0$ Hz, 1H), 4.41–4.27 (m, 2H), 4.17 (t, $J = 6.9$ Hz, 1H), 4.11–3.98 (m, 1H), 3.96–3.89 (m, 1H), 3.88–3.72 (m, 1H), 2.95–2.80 (m, 1H), 2.78–2.58 (m, 1H), 2.19 (d, $J = 6.3$ Hz, 1H), 2.10–2.00 (m, 1H), 1.95–1.77 (m, 1H), 1.75–1.58 (m, 1H), 0.86 (d, $J = 6.8$ Hz, 3H), 0.82 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.7, 156.3, 143.8, 143.7, 141.2, 141.1, 138.6, 133.4, 128.7, 128.3, 128.3, 127.5, 127.0, 125.8, 125.1, 125.0, 119.9, 72.4, 66.8, 57.1, 51.0, 47.4, 36.8, 32.0, 31.7, 20.3, 19.1. HRMS (ESI) calcd for $C_{36}H_{38}NO_4$ $[M + H]^+$ 548.2801, found 548.2803.

***syn*,*anti*-18b:** Colorless oil. IR (neat) 3415, 1716, 1663, 1513, 1248 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.63–7.25 (m, 9H), 5.98 (d, $J = 10.2$ Hz, 1H), 4.31–4.05 (m, 4H), 4.00–3.91 (m, 2H), 3.61 (t, $J = 9.2$ Hz, 1H), 2.05–1.92 (m, 1H), 1.88–1.75 (m, 1H), 1.09 (d, $J = 6.6$ Hz, 3H), 1.05 (d, $J = 6.4$ Hz, 3H), 0.99 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 204.1, 156.1, 144.1, 143.8, 141.2, 141.1, 136.4, 133.7, 128.9, 128.0, 127.5, 126.9, 125.1, 125.1, 119.8, 119.8, 77.3, 66.7, 58.2, 47.3, 45.6, 33.7, 31.7, 20.2, 19.9, 19.8. HRMS (ESI) calcd for $C_{31}H_{36}NO_4$ $[M + H]^+$ 486.2644, found 486.2645.

***anti*,*anti*-18b:** Colorless oil. IR (neat) 3410, 1706, 1507, 1240 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.99 (d, $J = 7.3$ Hz, 2H), 7.75 (d, $J = 7.3$ Hz, 2H), 7.62–7.25 (m, 9H), 6.11 (d, $J = 10.0$ Hz, 1H), 4.35 (d, $J = 6.9$ Hz, 2H), 4.19 (t, $J = 7.0$ Hz, 1H), 4.05 (dd, $J = 8.6$, 4.6 Hz, 1H), 3.96–3.88 (m, 1H), 3.77–3.56 (m, 1H), 2.07–1.95 (m, 1H), 1.92 (d, $J = 5.6$ Hz, 1H), 1.60–1.50 (m, 1H), 1.00 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.9$ Hz, 3H), 0.87 (d, $J = 6.9$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.5, 156.2, 143.9, 143.8, 141.2, 141.1, 139.0, 133.3, 128.6, 128.3, 127.5, 126.9, 125.0, 125.0, 119.8, 77.2, 66.7, 56.9, 47.8, 47.4, 32.1, 30.0, 20.2, 19.9, 19.1, 14.8. HRMS (ESI) calcd for $C_{31}H_{36}NO_4$ $[M + H]^+$ 486.2644, found 486.2636.

***syn*,*anti*-19a:** Colorless oil. IR (neat) 3343, 1694, 1449, 1248 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.67–6.97 (m, 19H), 6.65 (d, $J = 8.9$ Hz, 1H), 5.41–5.33 (m, 1H), 4.42–4.05 (m, 4H), 3.95–3.74 (m, 2H), 2.82–2.69 (m, 1H), 2.58–2.42 (m, 1H), 2.03–1.81 (m, 1H), 1.68–1.55 (m, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 202.8, 156.0, 143.7, 141.2, 140.2, 138.4, 133.8, 128.9, 128.8, 128.3, 128.2, 128.1, 127.6, 127.5, 126.9, 126.3, 125.7, 125.0, 119.8, 70.5, 67.0, 56.1, 53.3, 47.2, 38.3, 32.6. HRMS (ESI) calcd for $C_{39}H_{35}KNO_4$ $[M + K]^+$ 620.2203, found 620.2197.

***anti*,*anti*-19a:** Colorless oil. IR (neat) 3401, 1698, 1663, 1498, 1110 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.54–7.01 (m, 19H), 6.37 (d, $J = 8.7$ Hz, 1H), 5.31–5.24 (m, 1H), 4.33–4.20 (m, 3H), 4.12–4.00 (m, 2H), 2.95–2.80 (m, 1H), 2.70–2.40 (m, 2H), 1.91–1.32 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 205.4, 155.4, 143.6, 141.1, 140.0, 138.4, 133.4, 128.6, 128.4, 128.4, 128.3, 128.1, 127.5, 126.9, 126.9, 126.1, 125.9, 125.0, 119.8, 77.2, 71.8, 67.0, 55.2, 47.2, 37.0, 31.8. HRMS (ESI) calcd for $C_{39}H_{36}NO_4$ $[M + H]^+$ 582.2644, found 582.2664.

***syn*,*anti*-19b:** Colorless oil. IR (neat) 3402, 1704, 1449, 1248 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.77–6.97 (m, 16H), 5.42 (d, $J = 8.9$ Hz, 1H), 4.50–3.89 (m, 6H), 3.35 (t, $J = 9.6$ Hz, 1H), 1.80–1.60 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.69 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 203.3, 156.3, 143.7, 141.1, 136.2, 133.8, 133.2, 129.0, 128.8, 128.2, 127.5, 126.9, 126.1, 125.0, 119.8, 74.8, 66.9, 56.1, 52.5, 47.2, 32.3, 19.6, 15.5. HRMS (ESI) calcd for $C_{34}H_{34}NO_4$ $[M + H]^+$ 520.2488, found 520.2504.

***anti*,*anti*-19b:** Colorless oil. IR (neat) 3401, 1703, 1664, 1502, 1245 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.78–7.11 (m, 18H), 6.59 (d, $J = 8.6$ Hz, 1H), 5.20 (t, $J = 5.4$ Hz, 1H), 4.39–4.22 (m, 2H), 4.20–4.05 (m, 2H), 4.00–3.85 (m, 1H), 2.22 (brs, 1H), 2.10–1.91 (m, 1H), 1.03 (d, $J = 6.4$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 206.0, 155.5, 143.8, 141.1, 140.2, 138.7, 133.1, 128.6, 128.3, 128.0, 127.5, 127.4, 126.9, 126.0, 124.9, 119.9, 76.8, 66.9, 54.9, 52.5, 47.2, 30.4, 19.9, 15.5. HRMS (ESI) calcd for $C_{34}H_{34}NO_4$ $[M + H]^+$ 520.2488, found 520.2482.

(2*S*,3*R*)-2-Benzoyl-3-isopropylaziridine (22). The chiral aziridinyl ketone **22** was prepared according to the literature procedure.[13] $[\alpha]_D^{29} = -28.1$ (*c* 1.69, $CHCl_3$, 95.5% ee by the HPLC analysis), literature[13] $[\alpha]_D^{22} = -27.8$ (*c* 1.56, $CHCl_3$). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:19, 1.0 mL/min) t_R 5.50 min for the major enantiomer (9.08 min for the minor one).

(2*S*,3*R*)-2-Benzoyl-3-isopropyl-1-tosylaziridine (5). To a solution of 2-benzoyl-3-isopropylaziridine (**22**) (225 mg, 1.19 mmol) and DMAP (363 mg, 2.97 mmol) in CH_2Cl_2 (5 mL) was added TsCl (272 mg, 1.43 mmol) at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography to afford (2*S*,3*R*)-2-benzoyl-3-isopropyl-1-tosylaziridine (**5**) (253 mg, 62%). $[\alpha]_D^{28} = +37.5$ (*c* 0.96, $CHCl_3$).

(2*S*,3*R*,2′*S*)-5a: To a mixture of (2*S*,3*R*)-2-benzoyl-3-isopropyl-1-tosylaziridine (**5**) (49.2 mg, 0.143 mmol) and 3-phenylpropanal (21.1 mg, 0.158 mmol) in THF (3 mL) at −78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 3.6 mL, 0.36 mmol). After the reaction mixture was stirred for 1 h at −78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by thin-layer chromatography to afford (2*S*,3*R*,2′*S*)-**5a** (57.2 mg, 83%). $[\alpha]_D^{26} = +67.9$ (*c* 0.94, $CHCl_3$, 96.1% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:9, 1.0 mL/min) t_R 18.59 min for the major enantiomer (34.08 min for the minor one).

(2*S*,3*R*,2′*S*)-5b: $[\alpha]_D^{28} = +60.7$ (*c* 1.25, $CHCl_3$, 96.0% ee by the HPLC analysis). HPLC (CHIRALCEL OD, 2-propanol–hexane 1:9, 1.0 mL/min) t_R 14.32 min for the major enantiomer (12.42 min for the minor one).

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of γ,δ-Aziridinyl–α,β-Unsaturated Ester with Aldehyde. (Table 7, Entry 5). To a mixture of methyl (2*E*)-3-[(2*R*)-1-tosylaziridin-2-yl]acrylate (**23**) (49.5 mg, 0.176 mmol) and 3-phenylpropanal (26.0 mg, 0.194 mmol) in THF (4 mL) at −78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 4.4 mL, 0.44 mmol). After the reaction mixture was stirred for 30 min at −78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded *syn*-**23e** (36.0 mg, 49%) and *anti*-**23e** (34.6 mg, 47%), respectively.

***syn*-23a:** Colorless oil. IR (neat) 3500, 3282, 1732, 1328, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.33–7.25 (m, 7H), 5.74 (dd, $J = 15.4$, 9.2 Hz, 1H), 5.40 (dt, $J = 15.7$, 6.2 Hz, 1H), 5.02 (d, $J = 3.8$ Hz, 1H), 4.39 (t, $J = 5.9$ Hz, 1H), 3.59 (s, 3H), 3.51 (t, $J = 5.9$ Hz, 2H), 3.26 (dd, $J = 8.9$, 5.4 Hz, 1H), 2.90 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.5, 143.5, 140.4, 130.7, 129.7, 128.3, 128.2, 127.9, 127.0, 127.0, 126.1, 73.9, 56.6, 52.2, 44.9, 21.6. HRMS (ESI) calcd for $C_{20}H_{23}NNaO_5S$ $[M + Na]^+$ 412.1195, found 412.1204.

***anti*-23a:** Colorless oil. IR (neat) 3506, 3485, 1727, 1328, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.66 (d, $J = 8.1$ Hz, 2H), 7.36–7.22 (m, 7H), 5.48 (dd, $J = 15.7$, 8.6 Hz, 1H), 5.27 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.84 (dd, $J = 8.1$, 4.6 Hz, 1H), 4.25 (t, $J = 5.9$ Hz, 1H), 3.69 (s, 3H), 3.46–3.10 (m, 3H), 2.96 (d, $J = 4.9$ Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.8, 143.4, 140.7, 136.6, 129.9, 129.6, 128.3, 128.1, 127.6, 127.0, 126.4, 75.2, 56.4, 52.3, 44.8, 21.6. HRMS (ESI) calcd for $C_{20}H_{23}NNaO_5S$ $[M + Na]^+$ 412.1195, found 412.1173.

***syn*-23b:** Colorless oil. IR (neat) 3497, 3278, 1732, 1514, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.69 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 2H), 5.73 (dd, $J = 15.1$, 8.9 Hz, 1H), 5.43 (dt, $J = 14.9$, 5.4 Hz, 1H), 4.89 (d, $J = 6.2$ Hz, 1H), 4.78 (t, $J = 5.7$ Hz, 1H), 3.79 (s, 3H), 3.58–3.43 (m, 5H), 3.23 (dd, $J = 8.9$, 6.8 Hz, 1H), 2.98 (brs, 1H), 2.43 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.3, 159.0, 143.4, 136.5, 132.6, 130.6, 129.6, 127.4, 127.4, 127.0, 113.5, 73.7, 57.0, 55.2, 52.1, 44.8, 21.6. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_6S$ $[M + Na]^+$ 442.1300, found 442.1298.

***anti*-23b:** Colorless oil. IR (neat) 3498, 3281, 1732, 1497, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.66 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 6.8$ Hz, 2H), 6.84 (d, $J = 6.8$ Hz, 2H), 5.44 (dd, $J = 15.7$, 8.9 Hz, 1H), 5.25 (dt, $J = 15.7$, 6.2 Hz, 1H), 4.79 (dd, $J = 8.4$, 4.9 Hz, 1H), 4.36 (t, $J = 6.2$ Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.39 (t, $J = 6.2$ Hz, 2H), 3.31 (t, $J = 8.4$ Hz, 1H), 2.89 (d, $J = 4.6$ Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.9, 159.2, 143.4, 136.5, 132.8, 129.7, 129.6, 127.7, 127.6, 126.9, 113.6, 74.8, 56.5, 55.3, 52.2, 44.7, 21.6. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_6S$ $[M + Na]^+$ 442.1300, found 442.1304.

***syn*-23c:** Colorless oil. IR (neat) 3498, 3281, 1731, 1327, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.70 (d, $J = 7.8$ Hz, 2H), 7.33–7.14 (m, 6H), 5.71 (dd, $J = 15.7$, 9.5 Hz, 1H), 5.45 (dt, $J = 15.7$, 5.4 Hz, 1H), 4.96 (d, $J = 5.4$ Hz, 1H), 4.61 (t, $J = 5.9$ Hz, 1H), 3.59 (s, 3H), 3.53 (t, $J = 5.9$ Hz, 2H), 3.22 (dd, $J = 8.9$, 5.7 Hz, 1H), 3.11 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.3, 143.6, 138.9, 136.4, 133.5, 131.2, 129.7, 128.3, 127.5, 127.0, 126.5, 73.3, 56.6, 52.2, 44.8, 21.6. HRMS (ESI) calcd for $C_{20}H_{22}ClNNaO_5S$ $[M + Na]^+$ 446.0805, found 446.0814.

***anti*-23c:** Colorless oil. IR (neat) 3491, 3280, 1727, 1327, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.67 (d, $J = 8.4$ Hz, 2H), 7.31–7.14 (m, 6H), 5.48 (dd, $J = 15.4$, 8.9 Hz, 1H), 5.33 (dt, $J = 15.2$, 5.9 Hz, 1H), 4.82 (dd, $J = 7.3$, 4.9 Hz, 1H), 4.60 (t, $J = 6.2$ Hz, 1H), 3.68 (s, 3H), 3.42 (t, $J = 5.7$ Hz, 2H), 3.30 (t, $J = 8.4$ Hz, 1H), 3.18 (d, $J = 5.6$ Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.7, 143.5, 139.2, 136.5, 133.6, 130.3, 129.6, 128.4, 127.7, 126.9, 126.9, 74.4, 56.2, 52.3, 44.6, 21.6. HRMS (ESI) calcd for $C_{20}H_{22}ClNNaO_5S$ $[M + Na]^+$ 446.0805, found 446.0789.

***syn*-23d:** Colorless oil. IR (neat) 3502, 3279, 1731, 1327, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.72 (dd, $J = 15.7$, 8.9 Hz, 1H), 5.56 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.83 (t, $J = 5.9$ Hz, 1H), 3.84–3.75 (m, 1H), 3.69 (s, 3H), 3.57 (t, $J = 5.9$ Hz, 2H), 3.02 (dd, $J = 8.6$, 4.3 Hz, 1H), 2.43 (s, 3H), 1.46–1.28 (m, 2H), 0.92 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.4, 143.5, 136.6, 130.5, 129.6, 127.0, 127.0, 72.9, 53.8, 52.2, 45.0, 27.2, 21.6, 10.1. HRMS (ESI) calcd for $C_{16}H_{24}NO_5S$ $[M + H]^+$ 342.1375, found 342.1371.

***anti*-23d:** Colorless oil. IR (neat) 3506, 3279, 1730, 1328,

1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 5.63–5.54 (m, 2H), 4.68 (t, $J = 6.3$ Hz, 1H), 3.69 (s, 3H), 3.68–3.59 (m, 1H), 3.57 (t, $J = 5.7$ Hz, 2H), 3.07 (t, $J = 7.6$ Hz, 1H), 2.48–2.43 (m, 1H), 2.43 (s, 3H), 1.55–1.42 (m, 1H), 1.40–1.23 (m, 1H), 0.94 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.1, 143.5, 136.7, 129.7, 129.6, 128.1, 127.0, 73.8, 54.7, 52.1, 44.9, 27.6, 21.6, 9.9. HRMS (ESI) calcd for $C_{16}H_{24}NO_5S$ $[M + H]^+$ 342.1375, found 342.1372.

***syn*-23e:** Colorless oil. IR (neat) 3506, 3279, 1731, 1327, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.31–7.14 (m, 7H), 5.72 (dd, $J = 15.4$, 9.2 Hz, 1H), 5.57 (dt, $J = 15.7$, 5.4 Hz, 1H), 4.81 (t, $J = 6.2$ Hz, 1H), 3.89 (dt, $J = 8.9$, 4.3 Hz, 1H), 3.67 (s, 3H), 3.54 (t, $J = 5.7$ Hz, 2H), 3.01 (dd, $J = 8.9$, 4.3 Hz, 1H), 2.88–2.74 (m, 1H), 2.68–2.56 (m, 1H), 2.42 (s, 3H), 1.77–1.56 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.2, 143.5, 141.5, 136.8, 130.7, 129.7, 128.3, 128.3, 127.0, 126.9, 125.8, 70.7, 54.3, 52.2, 44.9, 36.0, 31.9, 21.6. HRMS (ESI) calcd for $C_{22}H_{28}NO_5S$ $[M + H]^+$ 418.1688, found 418.1710.

***anti*-23e:** Colorless oil. IR (neat) 3505, 3280, 1732, 1327, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.29–7.14 (m, 7H), 5.61 (dd, $J = 15.9$, 9.5 Hz, 1H), 5.56 (dt, $J = 15.9$, 5.9 Hz, 1H), 4.75 (t, $J = 6.2$ Hz, 1H), 3.81–3.68 (m, 1H), 3.67 (s, 3H), 3.56 (t, $J = 5.9$ Hz, 2H), 3.07 (t, $J = 7.3$ Hz, 1H), 2.88–2.76 (m, 1H), 2.69–2.56 (m, 1H), 2.41 (s, 3H), 1.77–1.57 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.2, 143.5, 141.5, 136.6, 129.8, 129.6, 128.3, 128.3, 127.8, 127.0, 125.8, 71.7, 55.0, 52.1, 44.9, 36.4, 31.8, 21.6. HRMS (ESI) calcd for $C_{22}H_{28}NO_5S$ $[M + H]^+$ 418.1688, found 418.1718.

***syn*-23f:** Colorless oil. IR (neat) 3520, 3280, 1731, 1328, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 5.73 (dd, $J = 15.7$, 9.2 Hz, 1H), 5.59 (dt, $J = 15.4$, 5.7 Hz, 1H), 4.81 (t, $J = 6.2$ Hz, 1H), 3.68 (s, 3H), 3.68–3.58 (m, 1H), 3.57 (t, $J = 6.2$ Hz, 2H), 3.18 (dd, $J = 8.6$, 4.3 Hz, 1H), 2.43 (s, 3H), 1.61–1.47 (m, 1H), 0.95 (d, $J = 6.8$ Hz, 3H), 0.78 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.6, 143.5, 136.6, 130.2, 129.6, 127.1, 127.0, 76.4, 52.2, 51.8, 45.0, 30.8, 21.6, 19.2, 17.8. HRMS (ESI) calcd for $C_{17}H_{26}NO_5S$ $[M + H]^+$ 356.1532, found 356.1522.

***anti*-23f:** Colorless oil. IR (neat) 3518, 3279, 1724, 1328, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.68–5.56 (m, 2H), 4.69 (t, $J = 6.5$ Hz, 1H), 3.69 (s, 3H), 3.56 (dd, $J = 6.2$, 4.6 Hz, 2H), 3.53–3.47 (m, 1H), 3.18 (t, $J = 7.8$ Hz, 1H), 2.43 (s, 3H), 1.68–1.57 (m, 1H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.85 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.4, 143.5, 136.7, 129.6, 129.1, 128.4, 127.0, 77.1, 52.5, 52.1, 44.9, 30.8, 21.6, 19.9, 15.8. HRMS (ESI) calcd for $C_{17}H_{26}NO_5S$ $[M + H]^+$ 356.1532, found 356.1515.

***syn*-23g:** Colorless oil. IR (neat) 3466, 3273, 1710, 1335, 1165 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.73 (dd, $J = 15.7$, 8.9 Hz, 1H), 5.58 (dt, $J = 15.4$, 5.7 Hz, 1H), 4.86 (t, $J = 6.2$ Hz, 1H), 3.68 (s, 3H), 3.64–3.58 (m, 1H), 3.57 (t, $J = 5.7$ Hz, 2H), 3.21 (dd, $J = 9.2$, 4.6 Hz, 1H), 2.69 (d, $J = 3.8$ Hz, 1H), 2.43 (s, 3H), 1.96–1.89 (m, 1H), 1.73–1.58 (m, 3H), 1.55–1.48 (m, 1H), 1.26–0.94 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.7, 143.4, 136.5, 130.1, 129.6, 127.1, 127.0, 75.5, 52.2, 51.2, 45.0, 40.2, 29.1, 28.2, 26.3, 26.0, 25.8, 21.6. HRMS (ESI) calcd for $C_{20}H_{30}NO_5S$ $[M + H]^+$ 396.1845, found 396.1855.

***anti*-23g:** Colorless oil. IR (neat) 3519, 3277, 1725, 1329, 1161 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.65 (dd, $J = 15.7$, 7.8 Hz, 1H), 5.55 (dt, $J = 15.4$, 5.4 Hz, 1H), 4.79 (t, $J = 6.2$ Hz, 1H), 3.68 (s, 3H), 3.56 (t, $J = 5.9$ Hz, 2H), 3.51–3.42 (m, 1H), 3.23 (t, $J = 7.8$ Hz, 1H), 2.52 (d, $J = 7.6$ Hz, 1H), 2.43 (s, 3H), 1.80–1.45 (m, 5H), 1.40–0.98 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.5, 143.4, 136.6, 129.6, 129.0, 128.6, 127.0, 76.8, 52.1, 51.6, 44.9, 40.8, 30.0, 26.5, 26.3, 26.2, 26.0, 21.6. HRMS (ESI) calcd for $C_{20}H_{30}NO_5S$ $[M + H]^+$ 396.1845, found 396.1850.

***syn*-23h:** Colorless oil. IR (neat) 3529, 3279, 1732, 1328, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.79 (dd, $J = 15.7$, 9.2 Hz, 1H), 5.59 (dt, $J = 15.4$, 6.2 Hz, 1H), 4.86 (t, $J = 6.2$ Hz, 1H), 3.66 (s, 3H), 3.65–3.58 (m, 1H), 3.55 (t, $J = 5.9$ Hz, 2H), 3.24 (dd, $J = 9.2$, 4.9 Hz, 1H), 2.59 (brs, 1H), 2.43 (s, 3H), 0.87 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.9, 143.4, 136.5, 130.6, 129.6, 128.6, 127.0, 78.0, 52.2, 51.0, 45.0, 35.6, 26.4, 21.6. HRMS (ESI) calcd for $C_{18}H_{27}NNaO_5S$ $[M + Na]^+$ 392.1508, found 392.1464.

***anti*-23h:** Colorless oil. IR (neat) 3512, 3278, 1717, 1329, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.79 (dd, $J = 15.4$, 8.1 Hz, 1H), 5.57 (dt, $J = 15.7$, 6.2 Hz, 1H), 4.82 (t, $J = 6.2$ Hz, 1H), 3.67 (s, 3H), 3.60–3.47 (m, 3H), 3.31–3.20 (m, 2H), 2.43 (s, 3H), 0.87 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.2, 143.4, 136.7, 130.6, 129.6, 128.2, 127.0, 81.4, 52.2, 48.5, 44.9, 36.0, 26.2, 21.6. HRMS (ESI) calcd for $C_{18}H_{27}NNaO_5S$ $[M + Na]^+$ 392.1508, found 392.1490.

Acetonide 24. To a solution of *syn*-**23e** (76 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) at -78 °C under an argon atmosphere was added a solution of DIBAL in toluene (1.1 M, 8.2 mL, 9 mmol). After the reaction mixture was stirred for 2 h at -20 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and then it was allowed to warm to 0 °C. The reaction mixture was made acidic with 5% HCl aq and extracted with CH_2Cl_2, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded *syn*-diol (48 mg, 68%). Colorless oil. IR (neat) 3478, 3294, 1324, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31–7.15 (m, 7H), 5.72 (dd, $J = 15.4$, 8.4 Hz, 1H), 5.55 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.95 (brs, 1H), 3.83–3.75 (m, 1H), 3.72 (d, $J = 5.4$ Hz, 2H), 3.56 (brs, 2H), 2.84–2.70 (m, 1H), 2.68–2.55 (m, 1H), 2.41 (s, 3H), 2.23–2.12 (m, 1H), 1.78–1.51 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.5, 141.6, 136.5, 129.9, 129.7, 129.0, 128.3, 127.0, 125.8, 72.5, 65.3, 49.3, 45.2, 37.0, 32.2, 21.6. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_4S$ $[M + Na]^+$ 412.1559, found 412.1532. To a solution of *syn*-diol (48 mg, 0.12 mmol) in 2,2-dimethoxypropane (2 mL) in CH_2Cl_2 (2 mL) at 0 °C was added 10-camphorsulfonic acid (CSA) (2 mg). After the reaction mixture was stirred for 2 h at room temperature, the reaction mixture was quenched with Et_3N. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded acetonide **24** (35 mg, 66%). Colorless oil. IR (neat) 3278, 1329, 1161 cm^{-1}. ^{1}H NMR (270 MHz, C_6D_6) δ 7.83 (d, $J = 8.2$ Hz, 2H), 7.32–7.16 (m, 5H), 6.89 (d, $J = 8.2$ Hz, 2H), 6.03 (dd, $J = 15.5$, 9.7 Hz, 1H), 5.30 (dt, $J = 15.6$, 6.1 Hz, 1H), 4.31 (t, $J = 6.1$ Hz, 1H), 3.76 (dd, $J = 11.3$, 2.8 Hz, 1H), 3.67 (ddd, $J = 8.9$, 4.0, 2.4 Hz, 1H), 3.52 (dd, $J = 11.4$, 1.6 Hz, 1H), 3.43 (dt, $J = 14.4$, 6.1 Hz, 1H), 3.36 (dt, $J = 14.4$, 6.4 Hz, 1H), 2.75

(ddd, $J = 13.8$, 8.9, 5.5 Hz, 1H), 2.63 (dt, $J = 13.8$, 8.3 Hz, 1H), 2.02 (s, 3H), 1.82 (ddt, $J = 14.0$, 5.2, 8.8 Hz, 1H), 1.57 (s, 3H), 1.44 (ddt, $J = 14.3$, 4.0, 7.9 Hz, 1H), 1.40–1.36 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.3, 141.5, 136.6, 131.8, 129.6, 128.4, 128.2, 127.0, 127.0, 125.8, 98.9, 69.8, 65.6, 45.5, 41.7, 35.3, 31.2, 29.7, 21.6, 19.1. HRMS (ESI) calcd for $C_{24}H_{31}NNaO_4S$ $[M + Na]^+$ 452.1872, found 452.1856.

Acetonide 25. To a solution of *anti*-**23e** (20.1 mg, 0.048 mmol) in CH_2Cl_2 (1 mL) at -78 °C under an argon atmosphere was added a solution of DIBAL in toluene (1.1 M, 0.2 mL, 0.22 mmol). After the reaction mixture was stirred for 2 h at -20 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and then it was allowed to warm at 0 °C. The reaction mixture was made acidic with 5% HCl aq and extracted with CH_2Cl_2, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded *anti*-diol (10.5 mg, 54%). Colorless oil. IR (neat) 3479, 3291, 1324, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.31–7.15 (m, 7H), 5.79–5.42 (m, 2H), 4.84 (brs, 1H), 3.78–3.65 (m, 3H), 3.52 (brs, 2H), 2.88–2.75 (m, 1H), 2.65–2.55 (m, 1H), 2.42 (s, 3H), 2.33–2.15 (m, 1H), 1.78–1.56 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.5, 141.7, 136.5, 131.6, 129.7, 128.4, 128.3, 128.2, 127.0, 125.8, 73.6, 64.6, 49.8, 45.1, 37.2, 31.9, 21.6. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_4S$ $[M + Na]^+$ 412.1559, found 412.1523. To a solution of *anti*-diol (10.0 mg, 0.026 mmol) in 2,2-dimethoxypropane (1 mL) and CH_2Cl_2 (1 mL) at 0 °C was added CSA (1 mg). After the reaction mixture was stirred for 2 h at room temperature, the reaction mixture was quenched with Et_3N. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded acetonide **25** (8.5 mg, 77%). Colorless oil. IR (neat) 3277, 1330, 1161 cm^{-1}. ^{1}H NMR (270 MHz, C_6D_6) δ 7.86 (d, $J = 8.2$ Hz, 2H), 7.31–7.24 (m, 4H), 7.17 (t, $J = 6.9$ Hz, 1H), 6.88 (d, $J = 7.9$ Hz, 2H), 5.06 (dt, $J = 15.2$, 7.8 Hz, 1H), 4.81 (dd, $J = 15.3$, 8.9 Hz, 1H), 4.62 (t, $J = 6.2$ Hz, 1H), 3.60 (dd, $J = 11.6$, 5.2 Hz, 1H), 3.48 (dt, $J = 2.4$, 9.8 Hz, 1H), 3.44 (t, $J = 11.3$ Hz, 1H), 3.30 (t, $J = 6.1$ Hz, 2H), 2.95 (ddd, $J = 13.8$, 9.2, 3.4 Hz, 1H), 2.78 (dt, $J = 13.5$, 8.3 Hz, 1H), 2.17 (dq, $J = 5.2$, 10.4 Hz, 1H), 2.00 (s, 3H), 1.89–1.83 (m, 1H), 1.72 (ddt, $J = 13.7$, 9.1, 4.5 Hz, 1H), 1.65 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.4, 141.9, 136.8, 129.9, 129.6, 128.6, 128.5, 128.2, 127.0, 125.6, 98.2, 71.1, 63.8, 45.0, 43.8, 35.3, 31.0, 29.7, 21.6, 19.1. HRMS (ESI) calcd for $C_{24}H_{31}NNaO_4S$ $[M + Na]^+$ 452.1872, found 452.1854.

23i (Less Polar Isomer): Colorless oil. IR (neat) 3508, 3281, 1731, 1330, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.31–7.12 (m, 7H), 5.76 (dd, $J = 15.1$, 9.7 Hz, 1H), 5.59 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.58 (t, $J = 6.5$ Hz, 1H), 3.69 (s, 3H), 3.55 (t, $J = 5.9$ Hz, 2H), 3.23 (brs, 1H), 3.09 (d, $J = 9.5$ Hz, 1H), 2.76–2.61 (m, 2H), 2.42 (s, 3H), 1.80–1.57 (m, 2H), 1.15 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.7, 143.5, 141.9, 130.4, 129.7, 128.3, 128.2, 127.8, 127.6, 127.0, 125.8, 73.2, 57.5, 52.2, 45.0, 43.3, 30.1, 23.6, 21.6. HRMS (ESI) calcd for $C_{23}H_{30}NO_5S$ $[M + H]^+$ 432.1845, found 432.1833.

23i (More Polar Isomer): Colorless oil. IR (neat) 3511, 3279, 1731, 1330, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.31–7.12 (m, 7H), 5.77 (dd, $J = 15.4$, 9.2 Hz, 1H), 5.58 (dt, $J = 15.1$, 6.2 Hz, 1H), 4.72 (t, $J = 6.2$ Hz, 1H), 3.70 (s, 3H), 3.56 (t, $J = 5.9$ Hz, 2H), 3.24 (brs, 1H), 3.09 (d, $J = 9.5$ Hz, 1H), 2.76–2.56 (m, 2H), 2.41 (s, 3H), 1.80–1.54 (m, 2H), 1.23 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.7, 141.9, 136.6, 130.5, 129.7, 128.3, 128.2, 127.7, 127.6, 127.0, 125.8, 73.0, 57.7, 52.1, 45.0, 41.2, 29.8, 25.3, 21.6. HRMS (ESI) calcd for $C_{23}H_{30}NO_5S$ $[M + H]^+$ 432.1845, found 432.1851.

23j: Colorless oil. IR (neat) 3508, 3279, 1731, 1329, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.75 (dd, $J = 15.7$, 9.4 Hz, 1H), 5.57 (dt, $J = 15.7$, 6.2 Hz, 1H), 4.77 (t, $J = 5.9$ Hz, 1H), 3.70 (s, 3H), 3.57 (t, $J = 6.2$ Hz, 2H), 3.16 (s, 1H), 2.98 (d, $J = 9.5$ Hz, 1H), 2.43 (s, 3H), 1.20 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.6, 143.5, 136.6, 130.3, 129.7, 128.0, 127.0, 71.4, 58.7, 52.0, 45.0, 28.5, 26.7, 21.6. HRMS (ESI) calcd for $C_{16}H_{24}NO_5S$ $[M + H]^+$ 342.1375, found 342.1381.

23k: Colorless oil. IR (neat) 3521, 3280, 1729, 1329, 1161 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 5.76 (dd, $J = 15.4$, 9.5 Hz, 1H), 5.58 (dt, $J = 15.4$, 5.9 Hz, 1H), 4.76 (t, $J = 6.2$ Hz, 1H), 3.69 (s, 3H), 3.54 (t, $J = 5.9$ Hz, 2H), 3.14 (s, 1H), 3.09 (d, $J = 5.9$ Hz, 1H), 2.43 (s, 3H), 1.81–1.19 (m, 4H), 0.84 (t, $J = 7.6$ Hz, 3H), 0.76 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.1, 143.4, 136.6, 129.9, 129.6, 127.9, 127.0, 75.4, 54.9, 52.0, 45.0, 29.5, 27.1, 21.6, 7.7, 7.4. HRMS (ESI) calcd for $C_{18}H_{28}NO_5S$ $[M + H]^+$ 370.1688, found 370.1693.

23l: Colorless oil. IR (neat) 3517, 3280, 1729, 1330, 1161 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.76 (dd, $J = 15.6$, 9.7 Hz, 1H), 5.55 (dt, $J = 15.7$, 6.2 Hz, 1H), 4.86 (t, $J = 6.2$ Hz, 1H), 3.68 (s, 3H), 3.56 (t, $J = 6.2$ Hz, 2H), 3.04 (s, 1H), 3.01 (d, $J = 9.5$ Hz, 1H), 2.43 (s, 3H), 1.62–1.32 (m, 8H), 1.29–1.15 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.7, 143.4, 136.6, 130.1, 129.6, 127.7, 127.0, 72.1, 57.7, 52.0, 45.0, 36.6, 34.7, 25.5, 21.8, 21.6, 21.5. HRMS (ESI) calcd for $C_{19}H_{28}NO_5S$ $[M + H]^+$ 382.1688, found 382.1707.

26a (Less Polar Isomer): Colorless oil. $[\alpha]_D^{23} = -111$ (*c* 0.82, $CHCl_3$). IR (neat) 3505, 3276, 1732, 1327, 1161 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 5.65 (dd, $J = 16.2$, 9.2 Hz, 1H), 5.51 (dd, $J = 15.7$, 6.5 Hz, 1H), 4.83 (dq, $J = 6.5$, 6.2 Hz, 1H), 4.61 (d, $J = 6.8$ Hz, 1H), 3.69 (s, 3H), 3.12 (s, 1H), 2.96 (d, $J = 9.2$ Hz, 1H), 2.43 (s, 3H), 1.19 (s, 3H), 1.18 (d, $J = 6.2$ Hz, 1H), 1.13 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.5, 143.4, 137.4, 136.6, 129.6, 127.0, 125.4, 71.4, 58.9, 52.0, 51.2, 28.1, 26.8, 21.8, 21.6. HRMS (ESI) calcd for $C_{17}H_{25}NNaO_5S$ $[M + Na]^+$ 378.1351, found 378.1319.

26a (More Polar Isomer): Colorless oil. $[\alpha]_D^{23} = +48.1$ (*c* 1.04, $CHCl_3$). IR (neat) 3509, 3277, 1732, 1327, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 5.64 (dd, $J = 15.4$, 9.5 Hz, 1H), 5.47 (dd, $J = 15.4$, 5.7 Hz, 1H), 4.80 (d, $J = 7.6$ Hz, 1H), 3.86 (dq, $J = 5.7$, 6.2 Hz, 1H), 3.71 (s, 3H), 3.11 (s, 1H), 2.92 (d, $J = 9.2$ Hz, 1H), 2.43 (s, 3H), 1.18 (d, $J = 6.2$ Hz, 1H), 1.16 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.6, 143.2, 137.6, 136.3, 129.5, 127.0, 125.1, 71.3, 58.7, 52.0, 50.8, 28.5, 26.6, 21.7, 21.6. HRMS (ESI) calcd for $C_{17}H_{25}NNaO_5S$ $[M + Na]^+$ 378.1351, found 378.1339.

Typical Procedure for the Preparation of γ,δ-Aziridinyl–α,β-Unsaturated Ester. To a solution of methyl (2*R*)-1-tosylaziridine-2-carboxylate (300 mg, 1.11 mmol) in CH_2Cl_2 (5 mL) at -78 °C under argon atmosphere was added a solution of

DIBAL in toluene (1.1 M, 1.23 mL, 1.23 mmol). After the reaction mixture was stirred for 1 h, NH_4Cl aq (1 mL) was added to it with stirring at −78 °C, followed by a solution of the sodium salt of diethylphosphonoacetic acid benzyl ester (0.48 M solution in DMF; 7 mL, 3.33 mmol). After the reaction mixture was stirred for 3 h, it was quenched with 1 M HCl aq. Then, it was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by column chromatography afforded benzyl ester **27** (235 mg, 59%).

Benzyl (2*E*)-3-[(2*R*)-1-Tosylaziridin-2-yl]acrylate (27): Colorless oil. $[\alpha]_D^{17} = -41.6$ (*c* 1.07, $CHCl_3$). IR (neat) 1721, 1328, 1163 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.81 (d, J = 8.1 Hz, 2H), 7.41–7.23 (m, 7H), 6.58 (dd, J = 15.4, 7.6 Hz, 1H), 6.15 (d, J = 15.7 Hz, 1H), 5.15 (s, 2H), 3.38–3.26 (m, 1H), 2.86 (d, J = 7.0 Hz, 1H), 2.44 (s, 3H), 2.26 (d, J = 3.2 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.9, 144.8, 142.1, 135.4, 134.3, 129.7, 128.4, 128.2, 128.2, 127.8, 124.8, 66.5, 38.5, 34.7, 21.8. HRMS (ESI) calcd for $C_{19}H_{19}NNaO_4S$ $[M + Na]^+$ 380.0933, found 380.0962.

***t*-Butyl (2*E*)-3-[(2*R*)-1-Tosylaziridin-2-yl]acrylate (28):** Colorless oil. $[\alpha]_D^{26} = -45.2$ (*c* 1.04, $CHCl_3$). IR (neat) 1714, 1659, 1321, 1163 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 6.43 (dd, J = 15.7, 7.6 Hz, 1H), 6.04 (d, J = 15.7 Hz, 1H), 3.38–3.31 (m, 1H), 2.85 (d, J = 7.0 Hz, 1H), 2.46 (s, 3H), 2.27 (d, J = 4.3 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.3, 144.8, 140.3, 134.4, 129.7, 127.8, 127.1, 81.0, 38.6, 34.6, 28.1, 21.7. HRMS (ESI) calcd for $C_{16}H_{21}NNaO_4S$ $[M + Na]^+$ 346.1089, found 346.1094.

Phenyl (2*E*)-3-[(2*R*)-1-Tosylaziridin-2-yl]acrylate (29): Colorless oil. $[\alpha]_D^{25} = -76.3$ (*c* 1.18, $CHCl_3$). IR (neat) 1738, 1328, 1162 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.39–7.34 (m, 4H), 7.23 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 7.3 Hz, 2H), 6.77 (dd, J = 15.7, 7.6 Hz, 1H), 6.33 (d, J = 15.7 Hz, 1H), 3.48–3.41 (m, 1H), 2.92 (d, J = 7.0 Hz, 1H), 2.47 (s, 3H), 2.34 (d, J = 4.3 Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.5, 150.2, 145.0, 143.6, 134.4, 129.8, 129.3, 127.9, 125.9, 124.4, 121.3, 38.4, 34.9, 21.8. HRMS (ESI) calcd for $C_{18}H_{17}NNaO_4S$ $[M + Na]^+$ 366.0776, found 366.0782.

2,6-Dimethylphenyl (2*E*)-3-[(2*R*)-1-Tosylaziridin-2-yl]acrylate (30): Colorless oil. $[\alpha]_D^{16} = -60.6$ (*c* 1.03, $CHCl_3$). IR (neat) 1736, 1329, 1163 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.05 (s, 3H), 6.81 (dd, J = 15.7, 7.3 Hz, 1H), 6.39 (d, J = 15.4 Hz, 1H), 3.52–3.41 (m, 1H), 2.91 (d, J = 7.0 Hz, 1H), 2.46 (s, 3H), 2.34 (d, J = 3.8 Hz, 1H), 2.11 (s, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 162.8, 147.7, 145.0, 143.7, 134.3, 129.9, 129.8, 128.4, 127.9, 125.9, 123.9, 38.3, 35.0, 21.8, 16.4. HRMS (ESI) calcd for $C_{20}H_{21}NNaO_4S$ $[M + Na]^+$ 394.1089, found 394.1108.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of γ,δ-Aziridinyl–α,β-Unsaturated Ester with Aldehyde. (Table 10, Entry 5). To a mixture of 2,6-dimethylphenyl (2*E*)-3-[(2*R*)-1-tosylaziridin-2-yl]acrylate (**30**) (56.1 mg, 0.151 mmol) and 3-phenylpropanal (24.3 mg, 0.181 mmol) in THF (3 mL) at −78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 3.8 mL, 0.38 mmol). After the reaction mixture was stirred for 30 min at −78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded *syn*-**30a** (64.9 mg, 87%) and *anti*-**30a** (7.2 mg, 10%), respectively.

***syn*-27a:** Colorless oil. IR (neat) 3516, 3281, 1730, 1328, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.34–7.05 (m, 12H), 5.73 (dd, J = 15.4, 8.9 Hz, 1H), 5.56 (dt, J = 15.4, 5.7 Hz, 1H), 5.09 (s, 2H), 4.88 (t, J = 5.7 Hz, 1H), 3.95–3.79 (m, 1H), 3.53 (t, J = 5.7 Hz, 2H), 3.04 (dd, J = 8.9, 4.6 Hz, 1H), 2.91–2.70 (m, 2H), 2.65–2.52 (m, 1H), 2.40 (s, 3H), 1.75–1.48 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.5, 143.4, 141.4, 136.4, 135.2, 130.8, 129.6, 128.6, 128.3, 128.3, 128.1, 127.0, 126.9, 125.8, 70.7, 66.8, 54.5, 44.9, 36.0, 31.9, 21.6. HRMS (ESI) calcd for $C_{28}H_{31}NNaO_5S$ $[M + Na]^+$ 516.1821, found 516.1800.

***anti*-27a:** Colorless oil. IR (neat) 3507, 3282, 1730, 1328, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.34–7.09 (m, 12H), 5.61 (dd, J = 15.7, 7.0 Hz, 1H), 5.54 (dt, J = 15.7, 5.2 Hz, 1H), 5.11 (s, 2H), 4.53 (t, J = 5.9 Hz, 1H), 3.81–3.69 (m, 1H), 3.51 (t, J = 5.1 Hz, 2H), 3.11 (t, J = 7.0 Hz, 1H), 2.85–2.74 (m, 1H), 2.69–2.48 (m, 1H), 2.40 (s, 3H), 1.79–1.56 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.3, 143.5, 141.4, 136.5, 135.3, 129.9, 129.6, 128.5, 128.3, 128.1, 127.8, 127.0, 125.8, 71.8, 66.7, 55.0, 44.9, 36.4, 31.8, 21.6. HRMS (ESI) calcd for $C_{28}H_{31}NNaO_5S$ $[M + Na]^+$ 516.1821, found 516.1804.

***syn*-28a:** Colorless oil. IR (neat) 3513, 3280, 1723, 1329, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.31–7.14 (m, 7H), 5.70 (dd, J = 15.1, 8.4 Hz, 1H), 5.56 (dt, J = 15.1, 6.2 Hz, 1H), 4.81 (t, J = 6.2 Hz, 1H), 3.91–3.79 (m, 1H), 3.55 (t, J = 6.2 Hz, 2H), 2.89 (dd, J = 8.4, 4.1 Hz, 1H), 2.85–2.55 (m, 2H), 2.41 (s, 3H), 1.79–1.55 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.2, 143.4, 141.6, 136.4, 130.2, 129.6, 128.3, 128.3, 127.6, 127.0, 125.8, 81.8, 70.7, 55.2, 45.1, 36.0, 31.9, 28.0, 21.6. HRMS (ESI) calcd for $C_{25}H_{33}NNaO_5S$ $[M + Na]^+$ 482.1977, found 482.1966.

***anti*-28a:** Colorless oil. IR (neat) 3504, 3280, 1723, 1329, 1158 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.30–7.14 (m, 7H), 5.62 (dd, J = 15.7, 7.3 Hz, 1H), 5.54 (dt, J = 15.4, 5.4 Hz, 1H), 4.62 (t, J = 5.7 Hz, 1H), 3.74–3.65 (m, 1H), 3.54 (t, J = 5.4 Hz, 2H), 2.96 (t, J = 7.6 Hz, 1H), 2.90–2.55 (m, 2H), 2.42 (s, 3H), 1.79–1.55 (m, 2H), 1.42 (s, 9H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.0, 143.4, 141.6, 136.5, 129.6, 129.2, 128.6, 128.4, 128.3, 127.0, 125.8, 81.9, 71.9, 55.5, 45.0, 36.6, 31.9, 28.1, 21.6. HRMS (ESI) calcd for $C_{25}H_{33}NNaO_5S$ $[M + Na]^+$ 482.1977, found 482.1966.

***syn*-29a:** Colorless oil. IR (neat) 3505, 3286, 1752, 1327, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.40–7.17 (m, 10H), 7.00 (d, J = 8.4 Hz, 2H), 5.84 (dd, J = 15.1, 8.9 Hz, 1H), 5.70 (dt, J = 15.1, 5.7 Hz, 1H), 4.89 (t, J = 5.7 Hz, 1H), 4.10–3.95 (m, 1H), 3.61 (t, J = 5.7 Hz, 2H), 3.24 (dd, J = 8.6, 4.6 Hz, 1H), 2.91–2.60 (m, 3H), 2.40 (s, 3H), 1.95–1.63 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.2, 150.1, 143.5, 141.4, 136.4, 131.4, 129.7, 129.4, 128.4, 127.0, 126.4, 126.0, 125.9, 121.2, 70.8, 54.6, 44.9, 36.2, 31.9, 21.6. HRMS (ESI) calcd for $C_{27}H_{29}NNaO_5S$ $[M + Na]^+$ 502.1664, found 502.1654.

***anti*-29a:** Colorless oil. IR (neat) 3507, 3285, 1753, 1327, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.40–7.10 (m, 10H), 7.01 (d, J = 8.4 Hz, 2H), 5.73 (dd, J = 15.7, 7.6 Hz, 1H), 5.67 (dt, J = 15.4, 5.4 Hz, 1H), 4.65 (t, J = 6.5 Hz, 1H), 3.95–3.80 (m, 1H), 3.59 (t, J = 5.2 Hz, 2H),

3.31 (t, $J = 7.6$ Hz, 1H), 2.93–2.80 (m, 1H), 2.75–2.60 (m, 1H), 2.52 (brs, 1H), 2.40 (s, 3H), 1.91–1.61 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.1, 150.1, 143.6, 141.4, 136.6, 130.6, 129.7, 129.4, 128.4, 128.4, 127.2, 127.0, 126.0, 125.9, 121.3, 71.8, 55.3, 44.9, 36.4, 31.9, 21.6. HRMS (ESI) calcd for $C_{27}H_{29}NNaO_5S$ $[M + Na]^+$ 502.1664, found 502.1657.

***syn*-30a:** Colorless oil. IR (neat) 3516, 3286, 1748, 1327, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.33–7.16 (m, 7H), 7.04 (s, 3H), 5.89 (dd, $J = 15.4$, 9.7 Hz, 1H), 5.76 (dt, $J = 15.1$, 6.3 Hz, 1H), 4.68 (t, $J = 5.4$ Hz, 1H), 4.13–4.04 (m, 1H), 3.62 (t, $J = 5.9$ Hz, 2H), 3.31 (dd, $J = 9.2$, 4.1 Hz, 1H), 2.88–2.80 (m, 1H), 2.76–2.62 (m, 1H), 2.40 (s, 3H), 2.06 (s, 6H), 1.85–1.65 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.5, 147.5, 143.5, 141.3, 136.4, 131.6, 129.8, 129.7, 128.5, 128.4, 128.3, 127.0, 126.5, 126.0, 125.9, 70.7, 54.5, 44.8, 36.3, 32.0, 21.6, 16.5. HRMS (ESI) calcd for $C_{29}H_{33}NNaO_5S$ $[M + Na]^+$ 530.1977, found 530.1988.

(2*E*)-1-Phenyl-3-[(2*R*)-1-tosylaziridin-2-yl]propenone (31). To a solution of methyl (2*R*)-1-tosylaziridine-2-carboxylate (500 mg, 1.96 mmol) in CH_2Cl_2 (7 mL) at -78 °C under argon atmosphere was added a solution of DIBAL in toluene (1.1 M, 2.2 mL, 2.4 mmol). After the reaction mixture was stirred for 1 h, NH_4Cl aq (1 mL) was added to it with stirring at -78 °C, followed by 2-(triphenylphosphoranylidene)acetophenone (820 mg, 2.4 mmol). After the reaction mixture was stirred for 3 h, it was quenched with 1 M HCl aq. Then, it was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by column chromatography afforded propenone **31** (430 mg, 67%). Colorless oil. $[\alpha]_D^{23} = -53.0$ (*c* 1.05, $CHCl_3$). IR (neat) 1624, 1320, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 8.1$ Hz, 2H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 15.4$, 1H), 6.66 (dd, $J = 15.4$, 7.6 Hz, 1H), 3.47 (ddd, $J = 7.6$, 7.0, 4.3 Hz, 1H), 2.93 (d, $J = 7.0$ Hz, 1H), 2.44 (s, 3H), 2.35 (d, $J = 4.3$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 188.8, 144.8, 141.3, 136.8, 134.4, 133.1, 129.7, 128.5, 128.5, 128.4, 127.8, 39.1, 35.0, 21.7. HRMS (ESI) calcd for $C_{18}H_{17}NNaO_3S$ $[M + Na]^+$ 350.0827, found 350.0849.

(2*E*)-*N*,*N*-Diethyl-3-[(2*R*)-1-tosylaziridin-2-yl]acrylamide (32). To a solution of methyl (2*E*)-3-[(2*R*)-1-tosylaziridin-2-yl]-acrylate (**23**) (300 mg, 1.78 mmol) in dioxane (2 mL)–MeOH (2 mL)–H_2O (1 mL) at 0 °C was added LiOH (123 mg, 5.34 mmol). After the reaction mixture was stirred for 4 h at room temperature, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. After evaporation of the solvent under reduced pressure, crude (2*E*)-3-[(2*R*)-1-tosylaziridin-2-yl]acrylic acid was obtained. To a mixture of crude (2*R*)-1-tosylaziridine-2-carboxylic acid (260 mg, 0.97 mmol), Et_2NH (140 mg, 1.94 mmol) in CH_2Cl_2 (5 mL) at 0 °C under argon atmosphere was added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDCI·HCl) (205 mg, 1.07 mol). After the reaction mixture was stirred for 2 h at room temperature, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by column chromatography afforded **32** (111 mg, 35%). Colorless oil. $[\alpha]_D^{21} = -47.5$ (*c* 1.16, $CHCl_3$). Colorless oil. IR (neat) 1617, 1326, 1161 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.59–6.44 (m, 2H), 3.44–3.27 (m, 5H), 2.87 (d, $J = 7.3$ Hz, 1H), 2.45 (s, 3H), 2.28 (d, $J = 4.3$ Hz, 1H), 1.15 (t, $J = 7.3$ Hz, 3H), 1.12 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 164.0, 144.7, 138.4, 134.5, 129.6, 127.7, 124.5, 42.2, 40.9, 39.3, 34.7, 21.7, 14.9, 13.0. HRMS (ESI) calcd for $C_{16}H_{23}N_2O_3S$ $[M + H]^+$ 323.1429, found 323.1451.

(2*E*)-1-Pyrrolidin-1-yl-3-[(2*R*)-1-tosylaziridin-2-yl]propenone (33). To a solution of crude (2*R*)-1-tosylaziridine-2-carboxylic acid (420 mg, 1.57 mmol) in THF (20 mL) at 0 °C under argon atmosphere was added Et_3N (428 mg, 4.23 mmol), pivaloyl chloride (PivCl) (257 mg, 2.13 mmol). After 45 min, pyrrolidine (223 mg, 3.13 mmol) was added to the reaction mixture, and it was allowed to warm at room temperature. After the reaction mixture was stirred for 1 h, it was quenched with H_2O. Then, it was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by column chromatography afforded **33** (350 mg, 70%). Colorless oil. $[\alpha]_D^{21} = -37.1$ (*c* 0.83, $CHCl_3$). IR (neat) 1621, 1450, 1321, 1162 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.82 (d, $J = 7.3$ Hz, 2H), 7.34 (d, $J = 7.3$ Hz, 2H), 6.53 (dd, $J = 15.1$, 7.0 Hz, 1H), 6.40 (d, $J = 14.9$ Hz, 1H), 3.52–3.43 (m, 4H), 3.35 (dt, $J = 4.3$, 7.0 Hz, 1H), 2.85 (d, $J = 7.0$ Hz, 1H), 2.44 (s, 3H), 2.27 (d, $J = 4.3$ Hz, 1H), 1.98–1.82 (m, 4H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.0, 144.7, 138.1, 134.6, 129.7, 127.8, 125.6, 46.6, 46.0, 39.2, 34.9, 26.1, 24.3, 21.8. HRMS (ESI) calcd for $C_{16}H_{21}N_2O_3S$ $[M + H]^+$ 321.1273, found 321.1250.

3-[(2*E*)-3-((2*R*)-1-Tosylaziridin-2-yl)acryloyl]oxazolidin-2-one (34). To a solution of crude (2*R*)-1-tosylaziridine-2-carboxylic acid (260 mg, 0.973 mmol) in THF (9 mL) at 0 °C under argon atmosphere was added Et_3N (294 mg, 2.92 mmol), PivCl (176 mg, 1.46 mmol). After 45 min, LiCl (212 mg, 5.00 mmol) and oxazolidin-2-one (127 mg, 1.46 mmol) was added to the reaction mixture, and it was allowed to warm at room temperature. After the reaction mixture was stirred for 1 h, it was quenched with H_2O. Then, it was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by column chromatography afforded **34** (168 mg, 52%). Colorless oil. $[\alpha]_D^{20} = -34.6$ (*c* 1.10, $CHCl_3$). IR (neat) 1777, 1685, 1388, 1162 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.54 (d, $J = 15.4$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 6.66 (dd, $J = 15.4$, 8.1 Hz, 1H), 4.43 (t, $J = 8.1$ Hz, 2H), 4.04 (t, $J = 8.1$ Hz, 2H), 3.42 (ddd, $J = 8.1$, 7.0, 4.3 Hz, 1H), 2.90 (d, $J = 7.0$ Hz, 1H), 2.45 (s, 3H), 2.34 (d, $J = 4.3$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.6, 153.1, 144.8, 143.2, 134.3, 129.7, 127.8, 123.6, 62.1, 42.6, 39.1, 34.5, 21.7. HRMS (ESI) calcd for $C_{15}H_{17}N_2O_5S$ $[M + H]^+$ 337.0858, found 337.0866.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of Unsaturated Aziridine with Aldehyde. (Table 11, Entry 4). To a mixture of 3-[(2*E*)-3-((2*R*)-1-tosylaziridin-2-yl)-acryloyl]oxazolidin-2-one (**34**) (22.0 mg, 0.066 mmol) and 3-phenylpropanal (10.0 mg, 0.075 mmol) in THF (3 mL) at -78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 1.6 mL, 0.16 mmol). After the reaction mixture was stirred for 30 min at -78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was di-

luted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded *syn*-**34a** (25.1 mg, 81%).

***syn*-31a:** Colorless oil. IR (neat) 3501, 3282, 1678, 1328, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.86 (d, $J = 7.3$ Hz, 2H), 7.68 (d, $J = 8.1$ Hz, 2H), 7.58 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.43–7.12 (m, 7H), 5.76 (dd, $J = 15.7$, 8.4 Hz, 1H), 5.64 (dt, $J = 15.9$, 5.7 Hz, 1H), 4.62 (t, $J = 5.9$ Hz, 1H), 4.10–3.92 (m, 2H), 3.53 (t, $J = 5.9$ Hz, 2H), 3.39 (brs, 1H), 2.95–2.77 (m, 1H), 2.75–2.61 (m, 1H), 2.40 (s, 3H), 1.94–1.65 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.4, 143.5, 141.6, 136.5, 135.7, 133.7, 131.4, 129.6, 128.7, 128.5, 128.4, 128.3, 128.0, 127.0, 125.8, 71.0, 54.8, 45.2, 36.2, 32.1, 21.6. HRMS (ESI) calcd for $C_{27}H_{29}NNaO_4S$ $[M + Na]^+$ 486.1715, found 486.1705.

***anti*-31a:** Colorless oil. IR (neat) 3500, 3279, 1679, 1328, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.88 (d, $J = 7.3$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.27–7.09 (m, 7H), 5.66 (dd, $J = 15.9$, 8.4 Hz, 1H), 5.54 (dt, $J = 15.7$, 5.1 Hz, 1H), 4.54 (t, $J = 5.7$ Hz, 1H), 4.10 (t, $J = 8.1$ Hz, 1H), 4.05–3.90 (m, 1H), 3.49 (t, $J = 5.7$ Hz, 2H), 3.01–2.77 (m, 2H), 2.75–2.56 (m, 1H), 2.40 (s, 3H), 1.91–1.67 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 201.2, 143.5, 141.6, 136.5, 136.4, 133.6, 130.2, 129.6, 129.2, 128.6, 128.5, 128.4, 128.3, 126.9, 125.8, 72.6, 55.7, 45.0, 36.5, 32.0, 21.6. HRMS (ESI) calcd for $C_{27}H_{29}NNaO_4S$ $[M + Na]^+$ 486.1715, found 486.1719.

***syn*-32a:** Colorless oil. IR (neat) 3280, 1615, 1329, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.31–7.15 (m, 7H), 5.75 (dd, $J = 15.7$, 8.9 Hz, 1H), 5.30 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.80 (t, $J = 6.2$ Hz, 1H), 3.75–3.60 (m, 1H), 3.54 (t, $J = 5.9$ Hz, 2H), 3.45–3.09 (m, 4H), 3.05 (dd, $J = 8.6$, 2.4 Hz, 1H), 2.89–2.74 (m, 1H), 2.73–2.58 (m, 2H), 2.42 (s, 3H), 1.93–1.72 (m, 2H), 1.12 (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.9, 143.4, 141.7, 136.4, 129.8, 129.7, 128.4, 128.3, 128.1, 127.0, 125.8, 71.2, 49.3, 45.2, 42.1, 40.5, 35.9, 32.1, 21.6, 14.7, 13.0. HRMS (ESI) calcd for $C_{25}H_{35}N_2O_4S$ $[M + H]^+$ 459.2318, found 459.2301.

***anti*-32a:** Colorless oil. IR (neat) 3465, 3275, 1614, 1329, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.34–7.14 (m, 7H), 5.73 (dd, $J = 15.7$, 8.1 Hz, 1H), 5.51 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.80 (t, $J = 6.5$ Hz, 1H), 4.33 (dd, $J = 8.1$, 2.2 Hz, 1H), 3.51 (t, $J = 5.9$ Hz, 2H), 3.45–3.15 (m, 4H), 3.14 (t, $J = 8.1$ Hz, 1H), 2.94–2.81 (m, 1H), 2.72–2.57 (m, 2H), 2.42 (s, 3H), 1.75–1.65 (m, 2H), 1.11 (t, $J = 7.3$ Hz, 3H), 1.10 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 172.1, 143.4, 141.9, 136.2, 130.7, 129.7, 128.4, 128.3, 128.2, 127.0, 125.8, 73.1, 50.1, 45.2, 42.1, 40.5, 34.4, 32.3, 21.6, 14.8, 13.1. HRMS (ESI) calcd for $C_{25}H_{35}N_2O_4S$ $[M + H]^+$ 459.2318, found 459.2299.

***syn*-33a:** Colorless oil. IR (neat) 3402, 3172, 1616, 1332, 1161 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.31–7.22 (m, 5H), 7.19 (d, $J = 8.1$ Hz, 2H), 5.73 (dd, $J = 15.4$, 8.9 Hz, 1H), 5.55 (dt, $J = 15.7$, 5.7 Hz, 1H), 5.01 (t, $J = 6.2$ Hz, 1H), 3.95–3.88 (m, 1H), 3.54 (t, $J = 5.9$ Hz, 2H), 3.53–3.33 (m, 4H), 2.95 (d, $J = 8.6$ Hz, 1H), 2.89–2.75 (m, 1H), 2.73–2.57 (m, 1H), 2.42 (s, 3H), 2.01–1.60 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.8, 143.4, 141.8, 136.4, 130.2, 129.6, 128.4, 128.2, 127.2, 127.0, 125.7, 70.6, 51.7, 46.5, 45.9, 45.2, 38.9, 32.0, 26.0, 24.2, 21.6. HRMS (ESI) calcd for $C_{25}H_{33}N_2O_4S$ $[M + H]^+$ 457.2161, found 457.2147.

***anti*-33a:** Colorless oil. IR (neat) 3275, 3176, 1616, 1329, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.31–7.23 (m, 5H), 7.18 (d, $J = 8.1$ Hz, 2H), 5.68 (dd, $J = 15.7$, 8.4 Hz, 1H), 5.53 (dt, $J = 15.7$, 5.7 Hz, 1H), 4.88 (t, $J = 5.2$ Hz, 1H), 3.76–3.65 (m, 1H), 3.51 (t, $J = 5.4$ Hz, 2H), 3.46–3.30 (m, 4H), 3.05 (t, $J = 5.9$ Hz, 1H), 2.95–2.82 (m, 1H), 2.69–2.54 (m, 1H), 2.42 (s, 3H), 1.95–1.60 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 171.1, 143.4, 142.0, 136.5, 129.7, 129.6, 128.6, 128.4, 128.3, 127.0, 125.7, 72.9, 52.7, 46.5, 45.8, 45.1, 37.1, 32.2, 25.9, 24.2, 21.6. HRMS (ESI) calcd for $C_{25}H_{33}N_2O_4S$ $[M + H]^+$ 457.2161, found 457.2171.

***syn*-34a:** Colorless oil. IR (neat) 3511, 3278, 1777, 1695, 1389, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.31–7.24 (m, 5H), 7.18 (d, $J = 8.1$ Hz, 2H), 5.82 (dd, $J = 15.7$, 9.2 Hz, 1H), 5.55 (dt, $J = 15.7$, 5.7 Hz, 1H), 5.00 (t, $J = 5.9$ Hz, 1H), 4.46 (dd, $J = 8.9$, 5.7 Hz, 1H), 4.43–4.37 (m, 2H), 4.08–3.90 (m, 3H), 3.54 (t, $J = 5.9$ Hz, 1H), 3.50 (t, $J = 5.4$ Hz, 1H), 3.36 (brs, 1H), 2.87–2.75 (m, 1H), 2.70–2.57 (m, 1H), 2.42 (s, 3H), 1.85–1.60 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.9, 152.9, 143.5, 141.5, 136.2, 131.1, 129.6, 128.4, 128.3, 127.0, 125.8, 125.6, 71.1, 62.1, 50.9, 44.9, 42.7, 36.1, 31.9, 21.6. HRMS (ESI) calcd for $C_{24}H_{28}N_2NaO_6S$ $[M + Na]^+$ 495.1566, found 495.1567.

Typical Procedure for the Preparation of γ,δ-Aziridinyl–α,β-Unsaturated Imide. To a solution of crude (2*R*)-1-tosylaziridine-2-carboxylic acid (690 mg, 2.58 mmol) in THF (25 mL) at 0 °C under argon atmosphere was added Et_3N (781 mg, 7.72 mmol), PivCl (468 mg, 3.88 mmol). After 45 min, LiCl (562 mg, 13.3 mmol) and oxazolidin-2-one (686 mg, 3.87 mmol) was added to the reaction mixture, and it was allowed to warm at room temperature. After the reaction mixture was stirred for 1 h, it was quenched with H_2O. Then, it was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by column chromatography afforded **35** (512 mg, 47%).

(4*R*)-4-Benzyl-3-[(2*E*)-3-((2*R*)-1-tosylaziridin-2-yl)acryloyl]-oxazolidin-2-one (35): Colorless oil. $[\alpha]_D^{22} = -67.3$ (*c* 1.00, $CHCl_3$). IR (neat) 1779, 1685, 1388, 1162 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.1$ Hz, 2H), 7.57 (d, $J = 15.1$ Hz, 1H), 7.38–7.25 (m, 5H), 7.18 (d, $J = 6.5$ Hz, 2H), 6.72 (dd, $J = 15.7$, 8.1 Hz, 1H), 4.73–4.64 (m, 1H), 4.25–4.14 (m, 2H), 3.44 (ddd, $J = 8.1$, 7.3, 4.3 Hz, 1H), 3.28 (dd, $J = 13.2$, 3.2 Hz, 1H), 2.93 (d, $J = 7.3$ Hz, 1H), 2.77 (dd, $J = 13.5$, 6.8 Hz, 1H), 2.45 (s, 3H), 2.36 (d, $J = 4.3$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.4, 153.0, 144.8, 143.5, 134.9, 134.3, 129.7, 129.3, 128.8, 127.8, 127.3, 124.1, 66.2, 55.2, 39.1, 37.7, 34.5, 21.7. HRMS (ESI) calcd for $C_{22}H_{22}N_2NaO_5S$ $[M + Na]^+$ 449.1147, found 449.1160.

(4*R*)-4-Benzyl-3-[(2*E*)-3-((2*R*,3*S*)-3-methyl-1-tosylaziridin-2-yl)acryloyl]oxazolidin-2-one (36): Colorless oil. $[\alpha]_D^{21} = -87.5$ (*c* 1.11, $CHCl_3$). IR (neat) 1780, 1684, 1390, 1161 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 15.4$ Hz, 1H), 7.37–7.15 (m, 7H), 6.83 (dd, $J = 15.4$, 7.6 Hz, 1H), 4.75–4.61 (m, 1H), 4.30–4.14 (m, 2H), 3.48 (t, $J = 7.3$ Hz, 1H), 3.31 (d, $J = 12.5$ Hz, 1H), 3.17 (dq, $J = 7.3$, 5.9 Hz, 1H), 2.77 (dd, $J = 13.2$, 9.5 Hz, 1H), 2.44 (s, 3H), 1.27 (d, $J = 5.7$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.4, 152.9, 144.5, 140.7, 134.9, 134.6, 129.6, 129.2, 128.8, 127.6, 127.2, 125.2, 66.2, 55.2, 43.9, 41.6, 37.7, 21.7, 12.6. HRMS (ESI) calcd

for $C_{23}H_{24}N_2NaO_5S$ $[M + Na]^+$ 463.1304, found 463.1315.

Typical Procedure for Samarium(II) Iodide-Mediated Aldol Reaction of Unsaturated Aziridine with Aldehyde. (Table 12, Entry 1). To a mixture of (4*R*)-4-Benzyl-3-[(2*E*)-3-((2*R*)-1-tosylaziridin-2-yl)acryloyl]oxazolidin-2-one (**35**) (43.0 mg, 0.098 mmol) and 3-phenylpropanal (14.5 mg, 0.11 mmol) in THF (3 mL) at −78 °C under an argon atmosphere was added a solution of SmI_2 in THF (0.1 M, 2.40 mL, 0.24 mmol). After the reaction mixture was stirred for 30 min at −78 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded *syn*-**35a** (51.3 mg, 93%).

***syn*-35a:** Colorless oil. $[\alpha]_D^{22} = -43.1$ (*c* 1.08, $CHCl_3$). IR (neat) 3509, 3280, 1780, 1697, 1390, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.30–7.15 (m, 12H), 5.82 (dd, $J = 15.7$, 8.6 Hz, 1H), 5.65 (dt, $J = 15.7$, 5.7 Hz, 1H), 4.88 (t, $J = 6.2$ Hz, 1H), 4.68–4.58 (m, 1H), 4.46 (dd, $J = 8.9$, 3.2 Hz, 1H), 4.25–4.08 (m, 2H), 4.03–3.92 (m, 1H), 3.53 (t, $J = 5.7$ Hz, 2H), 3.26 (dd, $J = 13.2$, 3.2 Hz, 1H), 3.19 (d, $J = 2.4$ Hz, 1H), 2.90–2.57 (m, 3H), 2.41 (s, 3H), 1.85–1.60 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.6, 152.8, 143.4, 141.5, 136.3, 134.9, 131.4, 129.6, 129.2, 128.9, 128.4, 128.3, 127.3, 127.0, 126.1, 125.8, 71.0, 66.2, 55.4, 50.9, 45.0, 38.0, 35.9, 31.9, 21.6. HRMS (ESI) calcd for $C_{31}H_{34}N_2NaO_6S$ $[M + Na]^+$ 585.2035, found 585.2064.

***syn*-35b:** Colorless oil. $[\alpha]_D^{15} = -61.3$ (*c* 1.12, $CHCl_3$). IR (neat) 3519, 3279, 1779, 1697, 1212, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.36–7.17 (m, 7H), 5.79 (dd, $J = 15.9$, 8.6 Hz, 1H), 5.67 (dt, $J = 15.4$, 5.4 Hz, 1H), 4.91 (t, $J = 5.7$ Hz, 1H), 4.69–4.60 (m, 1H), 4.48 (dd, $J = 8.6$, 3.5 Hz, 1H), 4.22 (t, $J = 8.4$ Hz, 1H), 4.15 (dd, $J = 8.9$, 2.2 Hz, 1H), 3.95–3.87 (m, 1H), 3.54 (t, $J = 5.4$ Hz, 2H), 3.29 (dd, $J = 13.2$, 3.2 Hz, 1H), 3.01 (brs, 1H), 2.76 (dd, $J = 13.0$, 9.5 Hz, 1H), 2.43 (s, 3H), 1.44 (dq, $J = 5.9$, 7.3 Hz, 2H), 0.95 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.6, 152.8, 143.4, 136.3, 134.9, 131.1, 129.6, 129.2, 128.9, 127.3, 127.0, 126.4, 73.2, 66.2, 55.4, 50.6, 45.0, 38.0, 27.2, 21.6, 10.2. HRMS (ESI) calcd for $C_{25}H_{30}N_2NaO_6S$ $[M + Na]^+$ 509.1722, found 509.1747.

***syn*-35c:** Colorless oil. $[\alpha]_D^{23} = -58.5$ (*c* 1.18, $CHCl_3$). IR (neat) 3521, 3277, 1780, 1695, 1389, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.36–7.17 (m, 7H), 5.79 (dd, $J = 15.4$, 8.6 Hz, 1H), 5.68 (dt, $J = 15.7$, 5.4 Hz, 1H), 4.84 (t, $J = 5.9$ Hz, 1H), 4.68 (dd, $J = 8.6$, 3.5 Hz, 1H), 4.67–4.60 (m, 1H), 4.23 (t, $J = 8.9$ Hz, 1H), 4.15 (dd, $J = 8.9$, 2.4 Hz, 1H), 3.67–3.57 (m, 1H), 3.55 (t, $J = 5.4$ Hz, 2H), 3.28 (dd, $J = 13.2$, 3.2 Hz, 1H), 2.96 (d, $J = 3.2$ Hz, 1H), 2.76 (dd, $J = 13.0$, 9.7 Hz, 1H), 2.43 (s, 3H), 1.65–1.52 (m, 1H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.9, 152.7, 143.4, 136.4, 134.9, 130.9, 129.6, 129.2, 128.9, 127.3, 127.1, 126.5, 76.7, 66.2, 55.3, 48.5, 45.1, 38.1, 31.2, 21.6, 19.0, 18.5. HRMS (ESI) calcd for $C_{26}H_{32}N_2NaO_6S$ $[M + Na]^+$ 523.1879, found 523.1886.

***syn*-35d:** Colorless oil. $[\alpha]_D^{19} = -42.7$ (*c* 1.03, $CHCl_3$). IR (neat) 3522, 3276, 1780, 1696, 1212, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.35–7.17 (m, 7H), 5.79 (dd, $J = 15.9$, 8.6 Hz, 1H), 5.66 (dt, $J = 15.7$, 5.1 Hz, 1H), 4.88 (t, $J = 5.9$ Hz, 1H), 4.72–4.60 (m, 2H), 4.27–4.05 (m, 2H), 3.75–3.62 (m, 1H), 3.54 (t, $J = 5.9$ Hz, 2H), 3.27 (dd, $J = 13.5$, 3.2 Hz, 1H), 2.76 (dd, $J = 13.2$, 9.7 Hz, 1H), 2.47 (s, 3H), 2.03–1.93 (m, 1H), 1.81–1.50 (m, 4H), 1.41–0.95 (m, 6H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.9, 152.7, 143.4, 136.3, 134.9, 130.7, 129.6, 129.2, 128.9, 127.3, 127.0, 126.6, 75.7, 66.2, 55.3, 48.1, 45.1, 40.5, 38.0, 28.9, 28.7, 26.3, 26.0, 25.9, 21.6. HRMS (ESI) calcd for $C_{29}H_{36}N_2NaO_6S$ $[M + Na]^+$ 563.2192, found 563.2204.

***syn*-36a:** Colorless oil. $[\alpha]_D^{18} = -84.9$ (*c* 1.05, $CHCl_3$). IR (neat) 3510, 3282, 1779, 1696, 1389, 1161 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.31–7.15 (m, 12H), 5.70 (dd, $J = 15.7$, 8.1 Hz, 1H), 5.60 (dt, $J = 15.7$, 5.7 Hz, 1H), 4.81 (d, $J = 6.5$ Hz, 1H), 4.73–4.58 (m, 1H), 4.44 (dd, $J = 8.1$, 4.1 Hz, 1H), 4.27–4.06 (m, 2H), 4.05–3.93 (m, 1H), 3.75–3.62 (m, 1H), 3.28 (dd, $J = 13.5$, 3.2 Hz, 1H), 3.21 (d, $J = 2.4$ Hz, 1H), 2.94–2.60 (m, 3H), 2.41 (s, 3H), 1.93–1.65 (m, 2H), 1.14 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.5, 152.9, 143.3, 141.7, 137.8, 137.1, 135.0, 129.7, 129.2, 128.8, 128.4, 128.3, 128.2, 127.0, 125.7, 123.7, 71.1, 66.2, 55.5, 51.3, 51.0, 38.0, 35.9, 31.9, 21.8, 21.6. HRMS (ESI) calcd for $C_{32}H_{36}N_2NaO_6S$ $[M + Na]^+$ 599.2192, found 599.2201.

***syn*-36b:** Colorless oil. $[\alpha]_D^{16} = -133$ (*c* 0.99, $CHCl_3$). IR (neat) 3520, 3280, 1780, 1695, 1389, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.40 (d, $J = 8.1$ Hz, 2H), 7.38–7.19 (m, 7H), 5.70 (dd, $J = 15.7$, 8.6 Hz, 1H), 5.66–5.59 (m, 1H), 4.71–4.60 (m, 3H), 4.24 (t, $J = 8.4$ Hz, 1H), 4.14 (dd, $J = 8.4$, 1.6 Hz, 1H), 3.81–3.70 (m, 1H), 3.69–3.60 (m, 1H), 3.31 (dd, $J = 13.0$, 3.0 Hz, 1H), 2.94 (d, $J = 2.4$ Hz, 1H), 2.75 (dd, $J = 13.2$, 10.0 Hz, 1H), 2.43 (s, 3H), 1.69–1.50 (m, 1H), 1.15 (d, $J = 6.8$ Hz, 3H), 0.99 (d, $J = 6.5$ Hz, 3H), 0.92 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.8, 152.8, 143.3, 137.3, 137.2, 135.0, 129.6, 129.2, 128.9, 127.3, 127.0, 124.0, 76.6, 66.2, 55.4, 51.3, 48.5, 38.1, 31.1, 21.9, 21.6, 19.3, 18.3. HRMS (ESI) calcd for $C_{27}H_{34}N_2NaO_6S$ $[M + Na]^+$ 537.2035, found 537.2022.

37: Colorless oil. $[\alpha]_D^{21} = -35.5$ (*c* 1.00, $CHCl_3$). IR (neat) 3264, 1782, 1689, 1388, 1159 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.37–7.24 (m, 5H), 7.18 (d, $J = 6.5$ Hz, 2H), 5.79 (dt, $J = 15.4$, 6.8 Hz, 1H), 5.55 (dt, $J = 15.4$, 6.2 Hz, 1H), 4.69–4.54 (m, 2H), 4.26–4.17 (m, 2H), 3.63 (d, $J = 6.8$ Hz, 2H), 3.60 (t, $J = 5.9$ Hz, 2H), 3.27 (dd, $J = 13.5$, 3.2 Hz, 1H), 2.75 (dd, $J = 13.2$, 9.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 170.6, 153.2, 143.4, 136.7, 134.9, 129.6, 129.2, 128.9, 127.3, 127.0, 125.3, 66.3, 55.1, 45.1, 38.7, 37.8, 21.6. HRMS (ESI) calcd for $C_{22}H_{24}N_2NaO_5S$ $[M + Na]^+$ 451.1304, found 451.1319.

(4*S*)-4-Benzyl-3-[(2*E*)-3-((2*R*,3*S*)-3-methyl-1-tosylaziridin-2-yl)acryloyl]oxazolidin-2-one (38): Colorless oil. $[\alpha]_D^{17} = -17.5$ (*c* 1.02, $CHCl_3$). IR (neat) 1781, 1684, 1389, 1161 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 15.1$ Hz, 1H), 7.37–7.15 (m, 7H), 6.83 (dd, $J = 15.7$, 7.3 Hz, 1H), 4.73–4.63 (m, 1H), 4.38–4.13 (m, 2H), 3.48 (t, $J = 7.6$ Hz, 1H), 3.30 (dd, $J = 13.8$, 3.2 Hz, 1H), 3.17 (dq, $J = 7.3$, 5.9 Hz, 1H), 2.77 (dd, $J = 13.2$, 9.5 Hz, 1H), 2.44 (s, 3H), 1.27 (d, $J = 5.9$ Hz, 1H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 163.4, 152.9, 144.5, 140.8, 134.9, 134.7, 129.7, 129.2, 128.8, 127.6, 127.2, 125.2, 66.2, 55.2, 43.9, 41.7, 37.7, 21.7, 12.6. HRMS (ESI) calcd for $C_{23}H_{24}N_2NaO_5S$ $[M + Na]^+$ 463.1304, found 463.1308.

***syn*-38a:** Colorless oil. $[\alpha]_D^{23} = -4.90$ (*c* 1.01, $CHCl_3$). IR (neat) 3517, 3275, 1779, 1697, 1389, 1160 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 7.69 (d, $J = 8.1$ Hz, 2H), 7.32–7.16 (m, 12H), 5.77–5.53 (m, 2H), 4.69 (d, $J = 6.2$ Hz, 1H), 4.67–4.58 (m, 1H), 4.55–4.45 (m, 1H), 4.25 (t, $J = 8.1$ Hz, 1H), 4.12 (d, $J =$

9.2 Hz, 1H), 4.05–3.98 (m, 1H), 3.77–3.65 (m, 1H), 3.27 (dd, $J = 13.5$, 3.2 Hz, 1H), 3.19 (brs, 1H), 2.90–2.58 (m, 3H), 2.40 (s, 3H), 1.78–1.54 (m, 2H), 1.14 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 173.7, 152.8, 143.3, 141.6, 137.5, 135.0, 129.6, 129.2, 128.8, 128.4, 128.3, 127.2, 127.0, 126.2, 125.8, 123.8, 70.8, 66.2, 55.6, 51.3, 50.6, 38.0, 35.9, 31.9, 21.6, 21.6. HRMS (ESI) calcd for $C_{32}H_{36}N_2NaO_6S$ $[M + Na]^+$ 599.2192, found 599.2167.

***syn*-38b:** Colorless oil. $[\alpha]_D^{22} = -2.42$ (c 0.96, $CHCl_3$). IR (neat) 3527, 3276, 1779, 1696, 1388, 1160 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.37–7.18 (m, 7H), 5.73–5.60 (m, 2H), 4.73–4.60 (m, 3H), 4.26 (t, $J = 8.6$ Hz, 1H), 4.14 (dd, $J = 8.1$, 1.6 Hz, 1H), 3.80–3.68 (m, 1H), 3.67–3.58 (m, 1H), 3.29 (dd, $J = 13.2$, 3.2 Hz, 1H), 2.95 (d, $J = 3.2$ Hz, 1H), 2.76 (dd, $J = 13.2$, 9.7 Hz, 1H), 2.42 (s, 3H), 1.61–1.48 (m, 1H), 1.15 (d, $J = 6.5$ Hz, 3H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.90 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 174.0, 152.9, 143.4, 137.2, 137.1, 135.0, 129.6, 129.3, 128.8, 127.3, 127.1, 124.1, 76.5, 66.2, 55.5, 51.3, 48.3, 38.1, 31.3, 21.7, 21.6, 19.0, 18.4. HRMS (ESI) calcd for $C_{27}H_{35}N_2O_6S$ $[M + H]^+$ 515.2216, found 515.2212.

(−)-*syn*-23e. To a solution of *syn*-**35a** (9.6 mg, 0.017 mmol) in MeOH (1 mL) at 0 °C was added NaOMe (0.1 mL, 28% in MeOH). After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous ammonium chloride and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded (−)-*syn*-**23e** (6.1 mg, 85%). Colorless oil. $[\alpha]_D^{21} = -27.0$ (c 0.26, $CHCl_3$).

(+)-MTPA Ester 39. To a solution of (−)-*syn*-**23e** (3.4 mg, 0.0081 mmol) in pyridine (1 mL) at 0 °C under an argon atmosphere was added DMAP (2 mg, 0.016 mmol) and (+)-MTPA-Cl (10 mg, 0.040 mmol). After the reaction mixture was stirred for 10 h at room temperature, the reaction mixture was quenched with H_2O and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded **39** (2.6 mg, 57%). Colorless oil. $[\alpha]_D^{19} = +17.4$ (c 0.17, $CHCl_3$). IR (neat) 3289, 1747, 1163 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.54 (brs, 2H), 7.42 (brs, 3H), 7.29–7.15 (m, 5H), 7.03 (d, $J = 6.8$ Hz, 2H), 5.60 (dd, $J = 15.1$, 8.4 Hz, 1H), 5.49 (dt, $J = 15.1$, 5.1 Hz, 1H), 5.44–5.38 (m, 1H), 4.34 (t, $J = 5.9$ Hz, 1H), 3.65 (s, 3H), 3.54 (s, 3H), 3.50 (t, $J = 5.4$ Hz, 2H), 3.30–3.23 (m, 1H), 2.50–2.43 (m, 2H), 2.42 (s, 3H), 1.95–1.70 (m, 2H). HRMS (ESI) calcd for $C_{32}H_{34}F_3NNaO_7S$ $[M + Na]^+$ 656.1906, found 656.1905.

(−)-MTPA Ester 40. To a solution of (−)-**23c** (5.3 mg, 0.013 mmol) in pyridine (1 mL) at 0 °C under an argon atmosphere was added DMAP (2.0 mg, 0.016 mmol) and (−)-MTPA-Cl (10 mg, 0.040 mmol). After the reaction mixture was stirred for 10 h at room temperature, the reaction mixture was quenched with H_2O and was diluted with ethyl acetate. It was extracted with ethyl acetate, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded **40** (5.5 mg, 78%). Colorless oil. $[\alpha]_D^{19} = -33.2$ (c 0.37, $CHCl_3$). IR (neat) 3286, 1747, 1162 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.55–4.48 (m, 2H), 7.45–7.37 (m, 3H), 7.34–7.15 (m, 5H), 7.09 (d, $J = 6.8$ Hz, 2H), 5.50 (dd, $J = 15.7$, 7.8 Hz, 1H), 5.45 (dt, $J = 15.7$, 5.4 Hz, 1H), 5.44–5.37 (m, 1H), 4.34 (t, $J = 6.2$ Hz, 1H), 3.64 (s, 3H), 3.56–3.43 (m, 5H), 3.25 (dd, $J = 8.4$, 5.7 Hz, 1H), 2.66–2.45 (m, 2H), 2.42 (s, 3H), 2.03–1.75 (m, 2H). HRMS (ESI) calcd for $C_{32}H_{34}F_3NNaO_7S$ $[M + Na]^+$ 656.1906, found 656.1885.

Carboxylic Acid 41. To a solution of *syn*-**35a** (9.0 mg, 0.022 mmol) in dioxane (1 mL) at 0 °C was added 30% H_2O_2 aq (0.03 mL, 0.256 mmol) and LiOH (1.5 mg, 0.065 mmol). After the reaction mixture was stirred for 3 h, the reaction mixture was quenched with Na_2SO_3 aq. The reaction mixture was made acidic with 5% HCl aq and extracted with ether, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded carboxylic acid **41** (7.0 mg, 80%). Colorless oil. $[\alpha]_D^{23} = -22.6$ (c 0.40, $CHCl_3$). IR (neat) 3283, 1581, 1159 cm^{-1}. ^{1}H NMR (270 MHz, CD_3OD) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.23–7.12 (m, 5H), 5.73 (dd, $J = 15.4$, 9.7 Hz, 1H), 5.57 (dt, $J = 15.1$, 5.9 Hz, 1H), 3.83–3.71 (m, 1H), 3.44 (d, $J = 5.9$ Hz, 2H), 2.88–2.70 (m, 2H), 2.66–2.50 (m, 1H), 2.41 (s, 3H), 1.77–1.53 (m, 2H). ^{13}C NMR (68 MHz, CD_3OD) δ 171.4, 145.2, 144.2, 139.5, 132.4, 131.4, 130.2, 130.0, 129.9, 128.8, 127.3, 73.6, 59.9, 48.7, 47.0, 34.0, 22.3. HRMS (ESI) calcd for $C_{21}H_{25}NNaO_5S$ $[M + Na]^+$ 426.1315, found 426.1366.

Diol 42. To a solution of *syn*-**35a** (8.2 mg, 0.0196 mmol) in EtOH (1 mL) at 0 °C was added $LiBH_4$ (2.0 M in THF, 0.1 mL, 0.2 mmol). After the reaction mixture was stirred for 2 h, the reaction mixture was quenched with saturated NH_4Cl aq. It was extracted with CH_2Cl_2, and the organic layer was washed with brine and dried over anhydrous sodium sulfate. The crude product was obtained after evaporation of the solvent under reduced pressure, and purification by thin-layer chromatography afforded diol **42** (5.7 mg, 75%). Colorless oil. $[\alpha]_D^{23} = -7.9$ (c 0.15, $CHCl_3$). IR (neat) 3478, 3294, 1324, 1158 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.31–7.15 (m, 7H), 5.74 (dd, $J = 15.4$, 8.4 Hz, 1H), 5.53 (dt, $J = 15.7$, 5.9 Hz, 1H), 4.80 (brs, 1H), 3.83–3.75 (m, 1H), 3.72 (d, $J = 5.4$ Hz, 2H), 3.56 (brs, 2H), 2.84–2.70 (m, 1H), 2.68–2.55 (m, 1H), 2.41 (s, 3H), 2.23–2.12 (m, 1H), 1.78–1.51 (m, 2H). ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.5, 141.6, 136.5, 129.9, 129.7, 129.0, 128.3, 127.0, 125.8, 72.5, 65.3, 49.3, 45.2, 37.0, 32.2, 21.6. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_4S$ $[M + Na]^+$ 412.1559, found 412.1532.

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References

1 For reviews of samarium(II) iodide in organic synthesis, see: a) G. A. Molander, *Chem. Rev.*, **92**, 29 (1992). b) G. A. Molander and C. R. Harris, *Chem. Rev.*, **96**, 307 (1996). c) G. A. Molander and C. R. Harris, *Tetrahedron*, **54**, 3321 (1998). d) P. G. Steel, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 2727.

2 G. A. Molander and G. Hahn, *J. Org. Chem.*, **51**, 1135 (1986).

3 G. A. Molander and G. Hahn, *J. Org. Chem.*, **51**, 2596

(1986).

4 a) K. Otsubo, J. Inanaga, and M. Yamaguchi, *Tetrahedron Lett.*, **28**, 4437 (1987). b) M. T. Reetz and E. H. Lauterbach, *Tetrahedron Lett.*, **32**, 4477 (1991). c) A. Bartelts, P. G. Jones, and J. Liebscher, *Tetrahedron: Asymmetry*, **6**, 1539 (1995).

5 a) G. A. Molander and P. J. Stengel, *J. Org. Chem.*, **60**, 6660 (1995). b) G. A. Molander and P. J. Stengel, *Tetrahedron*, **53**, 8887 (1997).

6 G. A. Molander, B. E. LaBelle, and G. Hahn, *J. Org. Chem.*, **51**, 5259 (1986).

7 a) T. Mukaiyama, H. Arai, and I. Shiina, *Chem. Lett.*, **2000**, 580. b) T. Mukaiyama, K. Pudhom, K. Yamane, and H. Arai, *Bull. Chem. Soc. Jpn.*, **76**, 413 (2003).

8 a) K. Pudhom, H. Arai, K. Yamane, and T. Mukaiyama, *Chem. Lett.*, **2002**, 87. b) J. Matsuo, Y. Ogawa, K. Pudhom, and T. Mukaiyama, *Chem. Lett.*, **33**, 124 (2004). c) Y. Ogawa, K. Kuroda, J. Matsuo, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, in press.

9 S. Abele and D. Seebach, *Eur. J. Org. Chem.*, **2000**, 1.

10 T. Mukaiyama, Y. Ogawa, and K. Kuroda, *Chem. Lett.*, **33**, 1472 (2004).

11 a) D. A. Evans, M. M. Faul, and M. T. Bilodeau, *J. Org. Chem.*, **56**, 6744 (1991). b) D. A. Evans, M. M. Faul, and M. T. Bilodeau, *J. Am. Chem. Soc.*, **116**, 2742 (1994).

12 D. L. Nagel, P. B. Woller, and N. H. Cromwell, *J. Org. Chem.*, **36**, 3911 (1971).

13 X. L. Jin, H. Sugihara, K. Daikai, H. Tateishi, Y. Z. Jin, H. Furuno, and J. Inanaga, *Tetrahedron*, **58**, 8321 (2002).

14 a) K. Kusuda, J. Inanaga, and M. Yamaguchi, *Tetrahedron Lett.*, **30**, 2945 (1989). b) E. J. Enholm and S. Jiang, *Tetrahedron Lett.*, **33**, 313 (1992).

15 a) R. Annunziata, M. Cinquini, F. Cozzi, and A. L. Borgia, *J. Org. Chem.*, **57**, 6339 (1992). b) G. P. Luke and J. Morris, *J. Org. Chem.*, **60**, 3013 (1995).

16 Y. Ogawa, K. Kuroda, and T. Mukaiyama, *Chem. Lett.*, **34**, 372 (2005).

17 S. Ohishi, T. Kamano, A. Niida, Y. Odagaki, N. Hamanaka, M. Yamamoto, K. Ajito, H. Tamamura, A. Otaka, and N. Fujii, *J. Org. Chem.*, **67**, 6162 (2002).

18 A. Otaka, A. Yukimasa, J. Watanabe, Y. Sasaki, S. Oishi, H. Tamamura, and N. Fujii, *Chem. Commun.*, **2003**, 1834.

19 N. Fujii, K. Nakai, H. Tamamura, A. Otaka, N. Mimura, Y. Miwa, T. Taga, Y. Yamamoto, and T. Ibuka, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 1359.

20 a) S. Fukuzawa, M. Tatsuzawa, and K. Hirano, *Tetrahedron Lett.*, **39**, 6899 (1998). b) S. Fukuzawa, H. Matsuzawa, and S. Yoshimitsu, *J. Org. Chem.*, **65**, 1702 (2000).

21 For reviews on chiral oxazolidinoe in asymmetric synthesis, see: a) D. J. Ager, I. Prakash, and D. R. Schaad, *Chem. Rev.*, **96**, 835 (1996). b) F. Velázquez and H. F. Olivo, *Curr. Org. Chem.*, **6**, 303 (2002).

22 I. Ohtani, T. Kusumi, Y. Kashman, and H. Kakisawa, *J. Am. Chem. Soc.*, **113**, 4092 (1991).

23 a) S. M. Yang and J. M. Fang, *Tetrahedron Lett.*, **38**, 1589 (1997). b) V. Reutrakul, R. Saeeng, M. Pohmakotr, and P. Kongsaeree, *Tetrahedron Lett.*, **40**, 1019 (1999). c) J. M. Concellón, P. L. Bernad, and H. Rodrígues-Solla, *Angew. Chem., Int. Ed.*, **40**, 3897 (2001).

24 M. Nerz-Stormes and E. R. Thornton, *J. Org. Chem.*, **56**, 2489 (1991).

25 D. A. Evans, E. B. Sjogren, J. Bartroli, and R. L. Dow, *Tetrahedron Lett.*, **27**, 4957 (1986).

26 P. Girard, J. L. Namy, and H. B. Kagan, *J. Am. Chem. Soc.*, **102**, 2693 (1980).