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Diastereoselective Aziridination of Chiral Electron-Deficient Olefins with *N*-Chloro-*N*-sodiocarbamates Catalyzed by Chiral Quaternary Ammonium Salts

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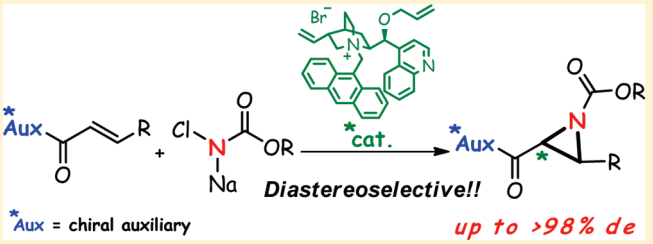
Supporting Information

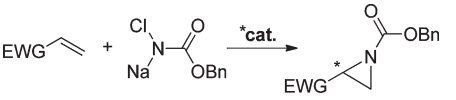
ABSTRACT: Chiral quaternary ammonium salt-catalyzed diastereoselective aziridination of electron-deficient olefins that possess a chiral auxiliary with *N*-chloro-*N*-sodiocarbamates was developed. The key to high stereoselectivity was found to be the employment of the "matching" stereochemical combination of chiral auxiliary/ammonium salt. For example, when 3-phenyl-(4*R*,7*S*)-4-methyl-7-isopropyl-4,5,6,7-tetrahydroindazole (L-menthopyrazole) as a chiral auxiliary and a cinchonidine-derived chiral ammonium salt as a catalyst were applied to the reaction system, perfect diastereoselectivity was realized. Furthermore, the preparation of enantiomerically pure aziridines by removal of the chiral auxiliary was demonstrated.



INTRODUCTION

Aziridines, three-membered aza-heterocycles, constitute an important class of biologically active compounds, such as azinomycin, porfiromycin, and mitomycin, which are potent antitumor or antibiotic agents.[1] Not only are aziridines biologically interesting components but they also serve as versatile building blocks in organic synthesis. For example, aziridines can be ring-opened with various nucleophiles to afford 1,2-difunctionalized products.[2] Some types of aziridines can also be transformed into useful products by rearrangement,[3] cycloaddition,[4] and carbonylative ring expansion reactions.[5] Therefore, tremendous effort has been devoted to the development of efficient and stereoselective synthetic methods for aziridines.[1,6] Among the myriad methods available, aziridination of olefins represents one of the most efficient approaches,[7] because aziridines are obtained in only a single step from readily available starting materials. Especially, aziridination of electron-deficient olefins such as α,β-unsaturated carbonyl compounds[8] should be useful, because the aziridinated products can be further derivatized. For example, ring-opening reaction of ester-substituted aziridines gives amino acid derivatives.[9] Hence, the developments of catalytic asymmetric variants have led to a breakthrough in this area. Evans and co-workers reported the first catalytic asymmetric nitrene transfer to α,β-unsaturated esters using a bis(oxazoline)−copper complex as a catalyst.[10] Although sufficient chemical yields and enantioselectivities were obtained by the reaction, the scope of the substrates were limited to cinnamate esters. Prabhakar and co-workers developed chiral ammonium salt-catalyzed enantioselective aziridination of α,β-unsaturated esters, sulfones, and sulfines.[11] Asymmetric aziridination of chalcones using a tertiary amine (Tröger's base or quinine) was reported by the Shi[7] and Armstrong groups.[12] The methods given above have shown great promise;

Scheme 1. Enantioselective Aziridination of Electron-Deficient Olefins with *N*-Chloro-*N*-sodiocarbamate



however, they require transition-metal catalysts or strong bases for the generation of the active nitrogen species. In this regard, organocatalytic asymmetric protocols have recently been reported, whereas the substrates were yet limited to α,β-unsaturated aldehydes[13] and ketones.[14] We have developed a new aziridination reaction of electron-deficient olefins such as α,β-unsaturated ketones, esters, sulfones, and amides with a chloramine salt, *N*-chloro-*N*-sodiocarbamate, in the presence of a phase-transfer catalyst.[15] Our preliminary investigation also showed that the reaction could be extended to the enantioselective version with the aid of a chiral ammonium salt, providing enantioenriched aziridines with good enantiomeric excess (ee) values up to 87% ee (Scheme 1). Nevertheless, the results do not meet the requirements of modern asymmetric synthesis in terms of enantioselectivity. We envisaged that introduction of chiral auxiliaries[16] to substrates should allow for more highly diastereoselective aziridination, and thus that literally enantiopure aziridines would be obtained by the removal of the auxiliaries (Scheme 2). Tardella and co-workers have reported chiral auxiliary-assisted diastereoselective aziridination using the combination of nosyloxycarbamates as a

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Scheme 2. Strategy for the Diastereoselective Aziridination of Chiral Electron-Deficient Olefins

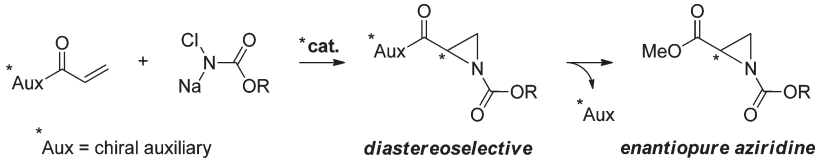
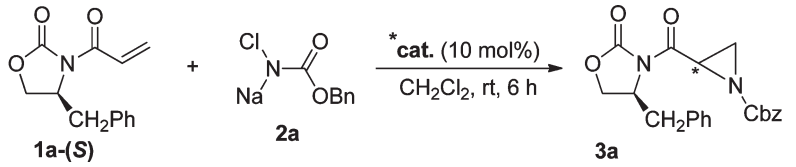
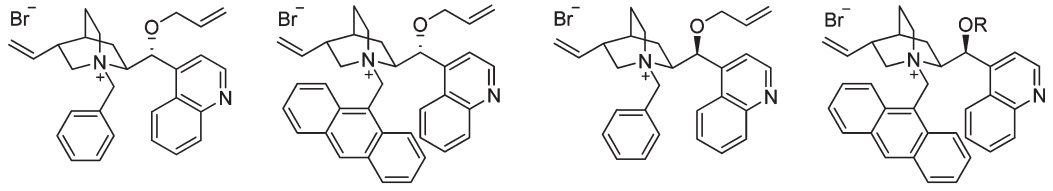


Table 1. Influence of Quaternary Ammonium Catalysts on the Aziridination Reaction of Chiral Electron-Deficient Olefin 1a-(*S*) with 2a[a]



*cat. =



entry	*cat. (10 mol %)	yield of **3a** (%)[b]	dr[c]
1	$Et_3(PhCH_2)N^+Cl^-$	83	57:43
2	**CD1**	90	41:59
3	**CD2**	80	42:58
4	**CN1**	88	76:24
5	**CN2**	87	81:19
6	**CN3**	89	79:21
7	**CN4**	94	80:20

[a] Reaction conditions: **1a**-(*S*) (0.15 mmol), **2a** (0.15 mmol), and *cat. (0.015 mmol) in CH_2Cl_2 (0.5 mL) at room temperature for 6 h. [b] Combined isolated yield. [c] Diastereomeric ratio of **3a**-(*S*,*R*):**3a**-(*S*,*S*) determined by ^1H NMR of the crude product.

nitrogen source and an inorganic base (CaO).[8k,17] Although their protocols were promising for production of highly enatioenriched azirizines, olefinic substrates were limited to alkenes bearing two geminal electron-withdrawing groups. Similarly, some types of *N*-amino heterocycles such as *N*-aminophthalimide, *N*-aminobenzimidazole, and 3-aminoquinazolinone have been applied to diastereoselective aziridination of chiral auxiliary-connected enone derivatives or utilized as a chiral nitrogen source.[18] However, the use of toxic $Pb(OAc)_4$ is indispensible for the reaction. Herein, we report a highly diastereoselective aziridination reaction of electron-deficient olefins having a chiral auxiliary, in which the concomitant use of a chiral ammonium catalyst is the key to achieving the high diastereoselectivity. Furthermore, the preparation of enantiopure aziridines was demonstrated.

RESULTS AND DISCUSSION

Oxazolidinone-type chiral auxiliaries[19] were initially chosen because α,β-unsaturated carbonyl compounds bearing an oxazolidinone auxiliary were smoothly aziridinated in our preliminary experiments.[15] The chiral auxiliaries used in this study were easily prepared from natural amino acids or readily available chiral amino alcohols. An acryloyl moiety was then introduced to the auxiliaries according to the procedure described in the literature.[20] With the enone derivatives bearing a chiral auxiliary in hand, we investigated the reaction of enone **1a**-(*S*) with chloramine salt **2a** in the presence of a quaternary ammonium salt at room temperature (Table 1). Although the reaction using an achiral phase-transfer catalyst $Et_3(PhCH_2)N^+Cl^-$ proceeded smoothly to give the corresponding aziridine **3a** in good yield, the diastereoselectivity was found to be very poor(entry 1). To improve stereoselectivity, a series of chiral ammonium salts, which were derived from cinchonidine or cinchonine, were examined as a catalyst. The reactions using chiral catalyst **CD1** or **CD2** yet resulted in very low diastereoselectivity in both cases (entries 2 and 3). The use of catalyst **CN1** was found to invert the sense of diastereoselectivity and resulted in higher stereoisomeric ratio, compared with the results of entries 2 and 3 (entry 4). The introduction of a bulkier substituent of an anthracenylmethyl group (**CN2**) on the quinuclidine nitrogen of the catalyst, instead of a benzyl group, improved

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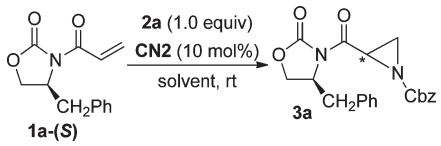
the diastereomeric ratio to 81:19 (entry 5). When the allyloxy group of **CN2** was replaced with benzyloxy (**CN3**) or propargyloxy (**CN4**) groups, the selectivities turned out to be almost the same with that obtained with catalyst **CN2** (entries 6 and 7).

Because the combination of a chiral auxiliary and chiral ammonium salt **CN2** was found to be the most effective in terms of the diastereomeric ratio of the product, solvent influence on the selectivity of the reaction was then investigated (Table 2). Among the solvents examined, nonpolar solvents proved to be effective for the reaction with respect to dr of the product; especially CH_2Cl_2 provided the best result (entries 1 and 2). Polar solvents such as THF and MeCN were ineffective, giving lower selectivities (entries 3 and 4).

In order to improve stereoselectivities, various enones bearing various chiral auxiliaries were examined (Table 3). When an enone having (*S*)-4-phenyl oxazolidinone moiety **1b**-(*S*) was employed as an auxiliary in place of the (*S*)-4-benzyl counterpart **1a**-(*S*), diastereoselectivity was slightly improved (entry 1). Chiral olefin **1b**-(*R*) was aziridinated with good diastereoselectivity when catalyst **CD2** (entry 2), which is a diastereomer of **CN2**, was employed, whereas the combination of chiral olefin **1b**-(*S*) and chiral catalyst **CN2** was necessary to induce higher diastereoselectivity. Both of the major diastereomers formed in

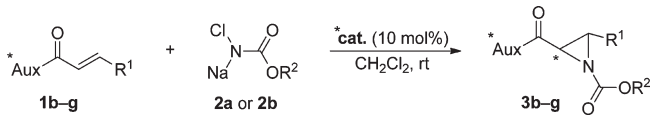
Table 2. Solvent Effect on Diastereoselectivity of the Aziridination of 1a-(*S*)[a]

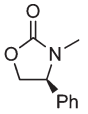
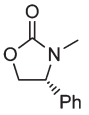
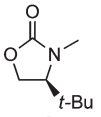
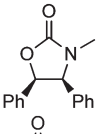
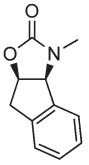
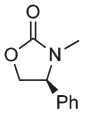
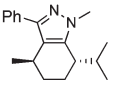


entry	solvent	time (h)	yield (%)[b]	dr[c]
1	CH_2Cl_2	6	87	81:19
2	toluene	6	91	78:22
3	THF	6	84	69:31
4	MeCN	3	83	58:42

[a] Reaction conditions: **1a**-(*S*) (0.15 mmol), **2a** (0.15 mmol), and **CN2** (0.015 mmol) in the corresponding solvent (0.5 mL) at room temperature. [b] Combined isolated yield. [c] Diastereomeric ratio of **3a**-(*S*,*R*):**3a**-(*S*,*S*) determined by ^{1}H NMR of the crude product.

Table 3. Diastereoselective Aziridination of Electron-Deficient Olefins Possessing a Chiral Auxiliary with Chloramine Salt[a]



entry	**1**	*Aux	R^1	R^2	***cat.**	**3**[b]	time (h)	yield (%)[c]	dr[d]
1	**1b-(*S*)**		H	CH_2Ph	**CN2**	**3b-(*S*,*R*)**	6	83	87:13
2	**1b-(*R*)**		H	CH_2Ph	**CD2**	**3b-(*R*,*S*)**	6	84	85:15
3	**1c-(*S*)**		H	CH_2Ph	**CN2**	**3c-(*S*,*R*)**	24	68	76:24
4	**1d-(*S*,*R*)**		H	CH_2Ph	**CN2**	**3d-(*S*,*R*,*R*)**	2	91	87:13
5	**1e-(*S*,*R*)**		H	CH_2Ph	**CN2**	**3e-(*S*,*R*,*R*)**	6	86	88:12
6	**1f-(*S*)**		CO_2Et	*t*-Bu	**CN2**	**3f-(*S*,*R*)**	24	60	76:24
7	**1g-(*R*,*S*)**		H	CH_2Ph	**CD2**	**3g-(*R*,*S*,*S*)**	9	84	89:11

[a] Reaction conditions: **1** (0.15 mmol), **2a** or **2b** (0.15 mmol), and *cat. (0.015 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. [b] Major diastereomer is indicated. [c] Combined isolated yield. [d] Diastereomeric ratios determined by ^{1}H NMR of the crude product.

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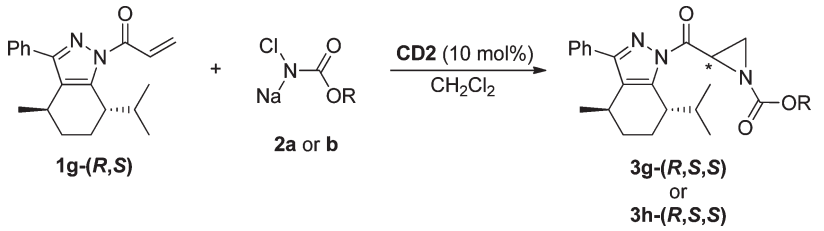
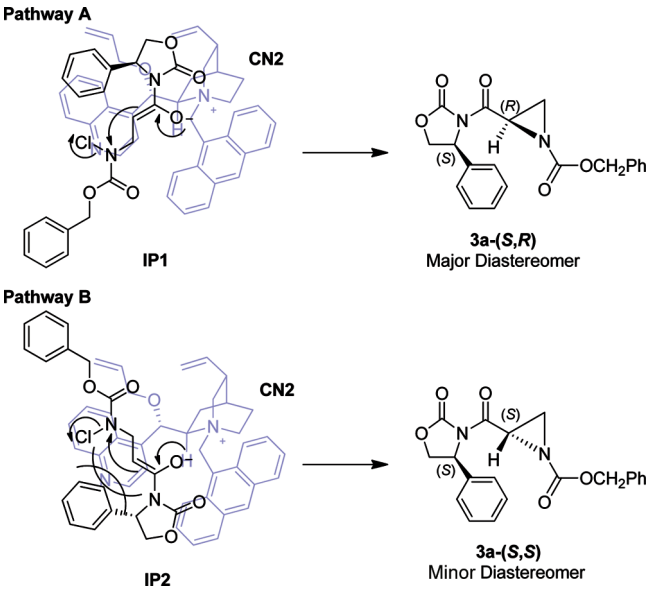
Table 4. Effect of Temperature on Diastereoselective Aziridination of 1g-(*R*,*S*)[a]



entry	R	temperature	time (h)	3[b]	yield (%)[c]	dr[d]
1	CH_2Ph	−20 °C	36	**3g**-(*R*,*S*,*S*)	75	95:5
2	*t*-Bu	rt	9	**3h**-(*R*,*S*,*S*)	90	94:6
3	*t*-Bu	−20 °C	36	**3h**-(*R*,*S*,*S*)	81	98:2
4	*t*-Bu	−40 °C	80	**3h**-(*R*,*S*,*S*)	77	>99:<1

[a] Reaction conditions: **1g**-(*R*,*S*) (0.15 mmol), **2a** or **2b** (0.15 mmol), and **CD2** (0.015 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. [b] Major diastereomer is indicated. [c] Combined isolated yield. [d] Diastereomeric ratios determined by ^{1}H NMR of the crude product.

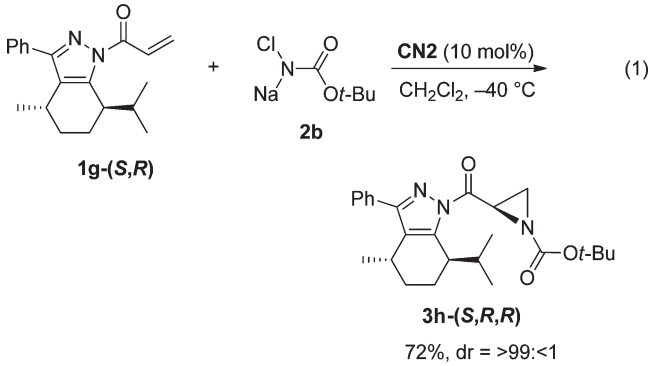
Scheme 3. Proposed Ion-Pairs for Diastereoselective Aziridination of 1b-(*S*)



the reaction of **1b**-(*S*) and **1b**-(*R*) were found to be the enantiomers of each other. Substitution of the phenyl moiety with a more sterically demanding substituent such as a *tert*-butyl group lowered both the reaction efficiency and dr (entry 3). Chiral enone **1d** possessing two phenyl groups and **1e**, which is the conformationally constrained analogue of **1b**-(*S*), reacted with chloramine salt **2a** to afford the corresponding aziridines **3d** and **3e** in high yield, while diastereomeric ratios were not improved (entries 4 and 5) compared with that obtained with **1b**-(*S*). Trans-disubstituted chiral enone **1f** was also converted to the desired aziridine **3f** with retention of the configuration around the olefinic bond by the reaction with *tert*-butyloxycarbonyl *N*-chloro-*N*-sodiocarbamate (**2b**) (entry 6).[21] In our previous study, we found that a series of pyrazole auxiliaries were effective to obtain high enantioselectivity in a similar reaction system. Therefore, a pyrazole-containing chiral auxiliary, L-menthopyrazole,[22] was also examined. Chiral enone **1g** was aziridinated by **2a** with good diastereoselectivity (entry 7).

Because the best result was obtained with the L-menthopyrazole auxiliary among the chiral auxiliaries surveyed, the influence of reaction temperature on the reaction of **1g**-(*R*,*S*) was then investigated (Table 4). At a lower temperature, higher stereoselectivity (95:5) was observed (entry 1). Notably, reaction efficiency was improved by employing *N*-Boc chloramine salt **2b** instead of *N*-Cbz chloramine salt **2a** (entry 2).[23] Furthermore, as the reaction temperature was lowered, diastereomeric ratio increased (entries 2−4), and perfect selectivity was achieved at −40 °C (entry 4).

Diastereoselective aziridination of enone **1g**-(*S*,*R*), which is the enantiomer of **1g**-(*R*,*S*), also successfully proceeded to give the corresponding aziridine **3h**-(*S*,*R*,*R*) in good yield (eq 1). Excellent diastereoselectivity was attained with the combination of chiral olefin **1g**-(*S*,*R*) and catalyst **CN2**. In this case, the product **3h**-(*S*,*R*,*R*) was the enantiomer of **3h**-(*R*,*S*,*S*).



(1)

In the reaction of (*S*)-configured chiral olefin **1b**-(*S*) with chloramine salt **2a** catalyzed by **CN2**, major diastereomer was found to be (*S*,*R*)-aziridine. To account for the observed stereochemical outcome, it could be reasonable to assume that a chiral ammonium salt/enolate ion pair is involved in this reaction (Scheme 3). According to the X-ray crystallographic data of **CD2** and modeling studies,[24] *N*-anthracenylmethylated quaternary ammonium salts would likely take a conformation where one of the tetrahedron faces formed by the ammonium group is blocked by the 9-anthracenylmethyl substituent, whose spatial position is fixed for steric reason. In addition, a bicyclic ring system and an allyloxy group would shield the two other faces of the tetrahedron, leaving the space above the remaining face open. Thus, the enolate approaches from the open face to

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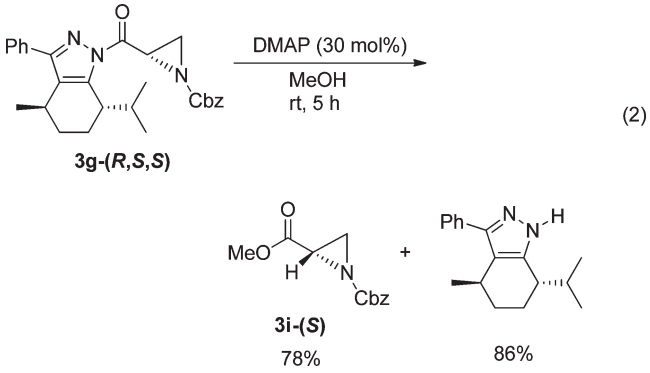
form the two possible ion pairs (**IP1** and **IP2**). The π-conjugation of the enolate could adopt a face to face $\pi-\pi$ interaction with the quinoline ring.[25] Cyclization from the opposite side of the quinoline moiety starting from **IP1** and **IP2** should give **3a**-(*S*,*R*) and **3a**-(*S*,*S*), respectively. In pathway A, the phenyl group at the C4 position of the oxazolidinone auxiliary is pointing up to avoid steric interactions with the rest of the substituents of the enolate and the ammonium catalyst. In pathway B, formation of the ion-pair **IP2** would be less favorable because of steric repulsion between the phenyl group of the chiral oxazolidinone and the ammonium catalyst.

In all cases, each of the diastereomers of aziridines **3** was readily separated by silica gel column chromatography. Moreover, the versatility of the method was demonstrated by preparation of enantiopure methyl ester-substituted aziridine **3h**-(*S*) from **3g**-(*R*,*S*,*S*) (eq 2). When **3g**-(*R*,*S*,*S*) was treated with MeOH in the presence of a catalytic amount of DMAP,[26] methanolysis of the acyl auxiliary proceeded smoothly to give enantiopure **3i**-(*S*) in 78% yield along with recovery of the chiral auxiliary in 86% yield.



3g-(*R*,*S*,*S*) (2)

3i-(*S*) 78%

86%

CONCLUSION

Chiral auxiliary-assisted diastereoselective aziridination of enones with *N*-chloro-*N*-sodiocarbamates has been developed. The aziridination was accelerated by a catalytic amount of a quaternary ammonium salt. The combination of a chiral auxiliary and a chiral ammonium salt with appropriate stereochemistry was crucial in terms of the diastereomeric ratio. The chiral auxiliary derived from menthol was found to be the most effective. This efficient and convenient method for diastereoselective aziridination could be a general method for the synthesis of enantiomerically pure aziridines. Further research is currently underway to synthesize natural or highly functionalized compounds using enantiopure aziridines.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out under a nitrogen atmosphere. Melting points were determined on a melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on an infrared spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a NMR spectrometer (^{1}H NMR, 270 MHz; ^{13}C NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured with a mass spectrometer. High resolution mass spectral data were obtained on a mass spectrometer. High performance liquid chromatography (HPLC) was performed using an LC system equipped with a chiral column and UV detector. Optical rotations were measured on a digital polarimeter. Flash column chromatography (FCC) was performed on silica gel. Preparative gel permeation chromatography (GPC) was performed with an LC system equipped with two polystyrene-gel columns using chloroform as an eluent. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualization was accomplished with UV light (254 nm) and spraying with an ethanolic phosphomolybdic acid solution followed by heating.

Typical Procedure for Diastereoselective Aziridination. A suspension of chiral olefin **1** (0.15 mmol), chloramine salt **2** (0.15 mmol), and ammonium catalyst (0.015 mmol) was stirred in CH_2Cl_2 (0.5 mL) for the durations indicated. The solution was then diluted with Et_2O (20 mL) and filtered, and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: hexane/AcOEt) to give the corresponding aziridines **3**.

Removal of the Chiral Auxiliary of 3g-(*R*,*S*,*S*). A solution of aziridine **3g**-(*R*,*S*,*S*) (35.5 mg, 0.09 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (3.3 mg, 0.03 mmol) was stirred in MeOH (0.5 mL) at room temperature for 5 h. The solvent was then evaporated under reduced pressure, and the resulting residue was immediately purified using silica gel column chromatography (eluent: hexane/AcOEt) to give the methyl ester-substituted aziridine **3i**-(*S*).

*(4S)-3-Acryloyl-4-benzyl-2-oxazolidinone [**1a-(S)**].* Spectroscopic data of compounds were in agreement with those for the previously reported material.[27] ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.81 (dd, 1H, J = 9.5, 13.5 Hz), 3.32 (dd, 1H, J = 3.2, 13.5 Hz), 4.16−4.26 (m, 2H), 4.69−4.78 (m, 1H), 5.93 (dd, 1H, J = 1.6, 10.5 Hz), 6.60 (dd, 1H, J = 1.6, 17.0 Hz), 7.20−7.36 (m, 5H), 7.51 (dd, 1H, J = 10.5, 17.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 37.7, 55.2, 66.2, 127.2, 128.8, 129.2, 131.7, 135.0, 153.1, 164.6

*(4S)-3-Acryloyl-4-phenyl-2-oxazolidinone [**1b-(S)**].* Spectroscopic data of compounds were in agreement with those for the previously reported material.[28] ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.31 (dd, 1H, J = 3.8, 8.9 Hz), 4.72 (dd, 1H, J = 8.9, 8.9 Hz), 5.49 (dd, 1H, J = 3.8, 8.9 Hz), 5.88 (dd, 1H, J = 1.6, 10.5 Hz), 6.48 (dd, 1H, J = 1.6, 16.7 Hz), 7.30−7.43 (m, 5H), 7.52 (dd, 1H, J = 10.5, 16.7 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 57.7, 70.1, 125.9, 127.0, 128.6, 129.1, 132.1, 138.6, 153.4, 164.2.

*(4R)-3-Acryloyl-4-phenyl-2-oxazolidinone [**1b-(R)**].* Spectroscopic data of compounds were in agreement with those for the previously reported material.[29] ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.30 (dd, 1H, J = 3.8, 8.9 Hz), 4.72 (dd, 1H, J = 8.9, 8.9 Hz), 5.49 (dd, 1H, J = 3.8, 8.9 Hz), 5.88 (dd, 1H, J = 1.6, 10.3 Hz), 6.48 (dd, 1H, J = 1.6, 17.0 Hz), 7.31−7.42 (m, 5H), 7.52 (dd, 1H, J = 10.3, 17.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 57.7, 70.0, 125.8, 127.0, 128.6, 129.1, 132.1, 138.6, 153.4, 164.2.

*(4S)-3-Acryloyl-4-tert-butyl-2-oxazolidinone [**1c-(S)**].* Spectroscopic data of compounds were in agreement with those for the previously reported material.[30] ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (s, 9H), 4.24−4.33 (m, 2H), 4.52 (dd, 1H, J = 2.4, 6.8 Hz), 5.91 (dd, 1H, J = 1.9, 10.5 Hz), 6.54 (dd, 1H, J = 1.9, 17.0 Hz), 7.53 (dd, 1H, J = 10.5, 17.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.6, 35.9, 60.8, 65.2, 127.2, 131.6, 154.3, 164.9.

*(4S,5R)-3-Acryloyl-4,5-diphenyl-2-oxazolidinone [**1d-(S,R)**].* Colorless solid; mp 117−119 °C; R_f = 0.33 (hexane/EtOAc, 7:3, v/v, silica gel plate); IR (KBr) 1695, 1768 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.73 (dd, 1H, J = 1.9, 10.5 Hz), 5.93(d, 1H, J = 10.3 Hz), 5.94 (d, 1H, J = 10.3 Hz), 6.53 (dd, 1H, J = 1.9, 17.0 Hz), 6.86−6.90 (m, 2H), 6.96−7.00 (m, 2H), 7.08−7.14 (m, 6H), 7.63 (dd, 1H, J = 10.5, 17.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 62.9, 80.4, 126.0, 126.5, 127.0, 127.9, 128.1, 128.2, 128.3, 132.3, 132.6, 134.1, 153.5, 164.0; MS (EI) m/z (relative intensity, %) 293 (M^+, 9), 249 (15), 132 (100), 77 (16), 55 (50); HRMS (EI) calcd for $C_{18}H_{15}NO_3$ (M)$^+$ 293.1053, found 293.1052; $[\alpha]^{16}_D$ −39.7 (c 0.95, $CHCl_3$).

*(3aS,8aR)-3-Acryloyl-3,3a,8,8a-tetrahydro-2H-indeno[1,2-d]oxazol-2-one [**1e-(S,R)**].* Colorless solid; mp 142−143 °C; R_f = 0.35 (hexane/EtOAc, 7:3, v/v, silica gel plate); IR (KBr) 1689, 1782 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.40−3.42 (m, 2H), 5.32 (ddd, 1H, J = 3.2, 4.1,

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7.0 Hz), 5.93 (dd, 1H, J = 1.6, 10.5 Hz), 6.01 (d, 1H, J = 7.0 Hz), 6.63 (dd, 1H, J = 1.6, 16.7 Hz), 7.26−7.36 (m, 3H), 7.51 (dd, 1H, J = 10.5, 16.7 Hz), 7.67 (d, 1H, J = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 37.9, 63.1, 78.1, 125.0, 127.1, 127.2, 127.9, 129.7, 131.7, 138.7, 139.2, 152.6, 165.0; MS (EI) m/z (relative intensity, %) 229 (M^+, 3), 185 (22), 157 (46), 130 (21), 77 (13), 55 (100); HRMS (EI) calcd for $C_{13}H_{11}N_1O_3$ $(M)^+$ 229.0739, found 229.0740; $[\alpha]^{16}_D$ +441.4 (c 0.99, $CHCl_3$).

*(4S)-3-{(E)-3-(Ethoxycarbonyl)propenyl}-4-phenyl-2-oxazolidinone [**1f-(S)**].* Colorless solid; mp 101−102 °C; R_f = 0.30 (hexane/EtOAc, 7:3, v/v, silica gel plate); IR (KBr) 1632, 1689, 1724, 1788 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.31 (t, 3H, J = 7.0 Hz), 4.26 (q, 2H, J = 7.0 Hz), 4.34 (dd, 1H, J = 3.8, 8.9 Hz), 4.76 (dd, 1H, J = 8.9, 8.9 Hz), 5.49 (dd, 1H, J = 3.8, 8.9 Hz), 6.86 (d, 1H, J = 15.5 Hz), 7.30−7.40 (m, 5H), 8.16 (d, 1H, J = 15.5 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.2, 57.8, 61.4, 70.2, 125.9, 128.9, 129.2, 131.9, 134.5, 138.1, 153.1, 163.1, 164.6; MS (EI) m/z (relative intensity, %) 289 (M^+, 7), 244 (9), 216 (82), 200 (7), 172 (17), 162 (100), 127 (43), 99 (48); HRMS (EI) calcd for $C_{15}H_{15}N_1O_5$ $(M)^+$ 289.0950, found 289.0952; $[\alpha]^{16}_D$ +81.8 (c 1.03, $CHCl_3$).

*(4R,7S)-1-Acryloyl-7-isopropyl-4-methyl-3-phenyl-4,5,6,7-tetrahydro-1H-indazole [**1g-(R,S)**].* Colorless oil; R_f = 0.40 (hexane/EtOAc, 9:1, v/v, silica gel plate); IR (neat) 1711 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89(d, 3H, J = 7.0 Hz), 0.93 (d, 3H, J = 7.0 Hz), 1.00 (d, 3H, J = 7.0), 1.45−1.51 (m, 1H), 1.78−1.85 (m, 2H), 2.02−2.24 (m, 2H), 3.18−3.24 (m, 1H), 3.45−3.50 (m, 1H), 5.96 (dd, 1H, J = 1.9, 10.3 Hz), 6.63 (dd, 1H, J = 1.9, 17.3 Hz), 7.39−7.47 (m, 3H), 7.73 (dd, 1H, J = 10.3, 17.3 Hz), 7.78−7.81 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.6, 19.8, 20.9, 21.3, 25.9, 27.3, 31.5, 38.1, 125.2, 127.5, 128.4, 128.5, 128.8, 131.1, 133.1, 146.1, 152.3, 164.7; MS (EI) m/z (relative intensity, %) 308 (M^+, 6), 265 (23), 253 (28), 211 (100); HRMS (EI) calcd for $C_{20}H_{24}N_2O$ $(M)^+$ 308.1890, found 308.1888; $[\alpha]^{15}_D$ −75.4 (c 1.44, $CHCl_3$).

*(4S,7R)-1-Acryloyl-7-isopropyl-4-methyl-3-phenyl-4,5,6,7-tetrahydro-1H-indazole [**1g-(S,R)**].* Colorless oil; R_f = 0.40 (hexane/EtOAc, 9:1, v/v, silica gel plate); IR (neat) 1711 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (d, 3H, J = 7.0 Hz), 0.93 (d, 3H, J = 7.0 Hz), 1.00 (d, 3H, J = 7.0), 1.45−1.52 (m, 1H), 1.79−1.85 (m, 2H), 2.02−2.24 (m, 2H), 3.18−3.24 (m, 1H), 3.45−3.50 (m, 1H), 5.96 (dd, 1H, J = 1.9, 10.3 Hz), 6.63 (dd, 1H, J = 1.9, 17.3 Hz), 7.39−7.48 (m, 3H), 7.73 (dd, 1H, J = 10.3, 17.3 Hz), 7.78−7.81 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.5, 19.7, 20.8, 21.2, 25.8, 27.2, 31.4, 38.0, 125.1, 127.4, 128.3, 128.4, 128.7, 131.0, 133.0, 146.0, 152.2, 164.6; MS (EI) m/z (relative intensity, %) 308 (M^+, 5), 265 (22), 253 (27), 211 (100); HRMS (EI) calcd for $C_{20}H_{24}N_2O$ $(M)^+$ 308.1890, found 308.1879; $[\alpha]^{15}_D$ +78.5 (c 0.92, $CHCl_3$).

*(4S)-4-Benzyl-3-[{(2′R)-(1′-benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-2-oxazolidinone [**3a-(S,R)**] (major isomer).* Colorless oil (49.9 mg, 87%, 81:19); R_f = 0.35 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1732, 1784 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.63 (dd, 1H, J = 1.6, 5.7 Hz), 2.68 (dd, 1H, J = 1.6, 3.2 Hz), 2.78 (dd, 1H, J = 9.7, 13.5 Hz), 3.25 (dd, 1H, J = 3.2, 13.5 Hz), 4.15−4.20 (m, 2H), 4.50−4.53 (m, 2H), 5.12 (d, 1H, J = 11.9 Hz), 5.26 (d, 1H, J = 11.9 Hz), 7.16−7.18 (m, 2H), 7.30−7.38 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.6, 34.0, 37.5, 55.4, 66.7, 68.5, 127.3, 127.9, 128.2, 128.3, 128.8, 129.1, 134.5, 135.2, 153.0, 160.5, 167.0; MS (EI) m/z (relative intensity, %) 380 (M^+, 7), 91 (100); HRMS (EI) calcd for $C_{21}H_{20}N_2O_5$ $(M)^+$ 380.1373, found 380.1371; $[\alpha]^{15}_D$ +76.8 (c 1.15, $CHCl_3$).

*(4S)-4-Benzyl-3-[{(2′S)-(1′-benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-2-oxazolidinone [**3a-(S,S)**] (minor isomer).* Colorless oil (49.9 mg, 87%, 81:19); R_f = 0.20 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1732, 1782 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.61 (dd, 1H, J = 1.6, 5.7 Hz), 2.64 (dd, 1H, J = 1.6, 3.2 Hz), 2.70 (dd, 1H, J = 9.2, 13.5 Hz), 3.17 (dd, 1H, J = 3.2, 13.5 Hz), 4.17−4.28 (m, 2H), 4.57 (dd, 1H, J = 3.2, 5.7 Hz), 4.64−4.70 (m, 1H), 5.18 (s, 2H), 7.14−7.17 (m, 2H), 7.26−7.40 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.7, 34.3, 37.5, 55.2, 66.6, 68.7, 127.3, 128.0, 128.3, 128.9, 129.3, 134.5, 135.1, 153.1, 160.7, 167.4; MS (EI) m/z (relative intensity, %) 380 (M^+, 5), 245 (6), 91 (100); HRMS (EI) calcd for $C_{21}H_{20}N_2O_5$ $(M)^+$ 380.1373, found 380.1374; $[\alpha]^{15}_D$ +23.8 (c 1.06, $CHCl_3$).

*(4S)-3-[{(2′R)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4-phenyl-2-oxazolidinone [**3b-(S,R)**] (major isomer).* Colorless oil (45.7 mg, 83%, 87:13); R_f = 0.35 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1732, 1784 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.51−2.53 (m, 2H), 4.27 (dd, 1H, J = 3.5, 8.9 Hz), 4.55 (dd, 1H, J = 3.5, 4.9 Hz), 4.60 (dd, 1H, J = 8.9, 8.9 Hz), 5.07 (d, 1H, J = 12.2 Hz), 5.18 (d, 1H, J = 12.2 Hz), 5.22 (dd, 1H, J = 3.5, 8.9 Hz), 7.23−7.26 (m, 2H), 7.32−7.36 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.5, 34.0, 57.7, 68.4, 70.4, 125.8, 128.2, 128.3, 128.4, 128.7, 129.0, 135.3, 138.0, 153.3, 160.5, 166.5; MS (EI) m/z (relative intensity, %) 366 (M^+, 9), 231 (3), 91 (100); HRMS (EI) calcd for $C_{20}H_{18}N_2O_5$ $(M)^+$ 366.1216, found 366.1219; $[\alpha]^{15}_D$ +139.6 (c 1.46, $CHCl_3$).

*(4S)-3-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4-phenyl-2-oxazolidinone [**3b-(S,S)**] (minor isomer).* Colorless solid (45.7 mg, 83%, 87:13); mp 122−123 °C; R_f = 0.20 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1720, 1794 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.54−2.58 (m, 2H), 4.34 (dd, 1H, J = 4.3, 8.9 Hz), 4.52 (dd, 1H, J = 3.2, 5.7 Hz), 4.69 (d, 1H, J = 12.2 Hz), 4.74 (dd, 1H, J = 8.9, 8.9 Hz), 5.09 (d, 1H, J = 12.2 Hz), 5.44 (dd, 1H, J = 4.3, 8.9 Hz), 7.16−7.19 (m, 2H), 7.28−7.33 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.7, 34.6, 57.8, 68.3, 70.5, 126.0, 128.0, 128.1, 128.3, 128.8, 129.1, 135.2, 137.8, 153.4, 160.7, 167.0; MS (EI) m/z (relative intensity, %) 366 (M^+, 13), 231 (2), 91 (100); HRMS (EI) calcd for $C_{20}H_{18}N_2O_5$ $(M)^+$ 366.1216, found 366.1214; $[\alpha]^{16}_D$ +60.4 (c 1.04, $CHCl_3$).

*(4R)-3-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4-phenyl-2-oxazolidinone [**3b-(R,S)**] (major isomer).* Colorless oil (46.1 mg, 84%, 85:15); R_f = 0.35 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1731, 1780 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.52−2.55 (m, 2H), 4.30 (dd, 1H, J = 3.5, 8.9 Hz), 4.56 (dd, 1H, J = 3.5, 5.1 Hz), 4.62 (dd, 1H, J = 8.9, 8.9 Hz), 5.08 (d, 1H, J = 11.9 Hz), 5.19 (d, 1H, J = 11.9 Hz), 5.22 (dd, 1H, J = 3.5, 8.9 Hz), 7.24−7.27 (m, 2H), 7.33−7.39 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.5, 33.9, 57.7, 68.4, 70.4, 76.4, 76.9, 77.4, 125.8, 128.2, 128.3, 128.7, 129.0, 135.2, 138.0, 153.2, 160.4, 166.5; MS (EI) m/z (relative intensity, %) 366 (M^+, 17), 260 (13), 218 (9), 104 (29), 91 (100); HRMS (EI) calcd for $C_{20}H_{18}N_2O_5$ $(M)^+$ 366.1216, found 366.1208; $[\alpha]^{15}_D$ −140.6 (c 0.87, $CHCl_3$).

*(4R)-3-[{(2′R)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4-phenyl-2-oxazolidinone [**3b-(R,R)**] (minor isomer).* Colorless solid (46.1 mg, 84%, 85:15); mp 123−124 °C; R_f = 0.20 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1720, 1792 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.54−2.58 (m, 2H), 4.32 (dd, 1H, J = 4.3, 8.9 Hz), 4.52 (dd, 1H, J = 3.2, 5.7 Hz), 4.68 (d, 1H, J = 12.2 Hz), 4.72 (dd, 1H, J = 8.9, 8.9 Hz), 5.09 (d, 1H, J = 12.2 Hz), 5.43 (dd, 1H, J = 4.3, 8.9 Hz), 7.15−7.19 (m, 2H), 7.28−7.33 (m, 8H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.6, 34.6, 57.8, 68.2, 70.5, 126.0, 128.0, 128.1, 128.3, 128.7, 129.0, 135.2, 137.8, 153.4, 160.7, 167.0; MS (EI) m/z (relative intensity, %) 366 (M^+, 16), 260 (16), 218 (11), 104 (33), 91 (100); HRMS (EI) calcd for $C_{20}H_{18}N_2O_5$ $(M)^+$ 366.1216, found 366.1219; $[\alpha]^{16}_D$ = −59.9 (c 0.73, $CHCl_3$).

*(4S)-3-[{(2′R)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4-tert-butyl-2-oxazolidinone [**3c-(S,R)**] (major isomer).* Colorless oil (35.5 mg, 68%, 76:24); R_f = 0.40 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1734, 1780 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.91 (s, 9H), 2.60 (dd, 1H, J = 1.6, 5.4 Hz), 2.67 (dd, 1H, J = 1.6, 3.2 Hz), 4.09 (dd, 1H, J = 7.6, 9.2 Hz), 4.26 (dd, 1H, J = 1.4, 9.2 Hz), 4.29 (dd, 1H, J = 1.4, 7.6 Hz), 4.58 (dd, 1H, J = 3.2, 5.4 Hz), 5.09 (d, 1H, J = 12.2 Hz), 5.18 (d, 1H, J = 12.2 Hz), 7.34−7.38 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.6, 32.8, 33.8, 35.8, 61.6, 65.8, 68.5, 128.2, 128.3, 128.4, 135.3, 154.3, 160.6, 167.2; MS (EI) m/z (relative intensity, %) 346 (M^+, 7), 91 (100); HRMS (EI) calcd for $C_{18}H_{22}N_2O_5$ $(M)^+$ 346.1530, found 346.1524; $[\alpha]^{15}_D$ +85.2 (c 1.43, $CHCl_3$).

*(4S)-3-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4-tert-butyl-2-oxazolidinone [**3c-(S,S)**] (minor isomer).* Colorless oil (35.5 mg, 68%, 76:24); R_f = 0.25 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1732, 1780 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (s, 9H), 2.54 (dd, 1H, J = 1.6, 3.0 Hz), 2.58 (dd, 1H, J = 1.6, 5.7 Hz), 4.25−4.36 (m, 2H), 4.43 (dd, 1H, J = 1.9, 7.3 Hz), 5.05 (d, 1H, J = 12.2 Hz), 5.24 (d, 1H, J = 12.2 Hz), 7.35−7.40 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.5, 32.7, 34.8, 35.8, 61.2, 65.7, 68.5, 128.2, 128.4, 135.2, 154.2, 160.7, 167.7; MS (EI) m/z (relative intensity, %) 346 (M^+, 6), 91 (100); HRMS (EI) calcd for $C_{18}H_{22}N_2O_5$ $(M)^+$ 346.1530, found 346.1526; $[\alpha]^{15}_D$ +9.4 (c 0.89, $CHCl_3$).

*(4S,5R)-3-[{(2′R)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4,5-diphenyl-2-oxazolidinone [**3d-(S,R,R)**] (major isomer).* Colorless solid (60.1 mg, 91%, 87:13); mp 52−53 °C; R_f = 0.45 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1730, 1784 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.59−2.62 (m, 2H), 4.65 (dd, 1H, J = 3.5, 4.9 Hz), 5.10 (d, 1H, J = 12.2 Hz), 5.22 (d, 1H, J = 12.2 Hz), 5.44 (d, 1H, J = 7.6 Hz), 5.81 (d, 1H, 7.6 Hz), 6.80−6.84 (m, 2H), 6.92−6.96 (m, 2H), 7.08−7.14 (m, 6H), 7.32−7.41 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.7, 34.1, 63.1, 68.5, 80.9, 125.9, 126.3, 128.0, 128.3, 128.4, 128.5, 128.6, 132.1, 133.5, 135.4, 153.4, 160.5, 166.4; MS (EI) m/z (relative intensity, %) 442 (M^+, 1), 180 (98), 91 (100); HRMS (EI) calcd for $C_{26}H_{22}N_2O_5$ $(M)^+$ 442.1530, found 442.1528; $[\alpha]^{15}_D$ +53.6 (c 1.42, $CHCl_3$).

*(4S,5R)-3-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-4,5-diphenyl-2-oxazolidinone [**3d-(S,R,S)**] (minor isomer).* Colorless solid (60.1 mg, 91%, 87:13); mp 198−199 °C; R_f = 0.20 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1714, 1788 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.61−2.63 (m, 2H), 4.68 (dd, 1H, J = 3.2, 5.1 Hz), 4.73 (d, 1H, J = 12.2 Hz), 5.10 (d, 1H, J = 12.2 Hz), 5.70 (d, 1H, J = 7.6 Hz), 5.96 (d, 1H, 7.6 Hz), 6.87−6.90 (m, 2H), 6.96−6.98 (m, 2H), 7.01−7.29 (m, 11H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.7, 34.6, 62.9, 68.3, 80.8, 126.0, 126.5, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 132.2, 133.4, 135.2, 153.4, 160.7, 166.8; MS (EI) m/z (relative intensity, %) 442 (M^+, 1), 180 (100), 91 (81); HRMS (EI) calcd for $C_{26}H_{22}N_2O_5$ $(M)^+$ 442.1530, found 442.1527; $[\alpha]^{16}_D$ −22.2 (c 1.32, $CHCl_3$).

*(3aS-cis)-3-[{(2′R)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-3,3a,8,8a-tetrahydro-2H-indeno[1,2-d]-2-oxazolidinone [**3e-(S,R,R)**] (major isomer).* Colorless solid (48.7 mg, 86%, 88:12); mp 45−46 °C; R_f = 0.35 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1732, 1782 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.60 (dd, 1H, J = 1.9, 5.7 Hz), 2.67 (dd, 1H, J = 1.9, 3.2 Hz), 3.38−3.40 (m, 2H), 4.52 (dd, 1H, J = 3.2, 5.7 Hz), 5.15 (d, 1H, J = 11.9 Hz), 5.21 (d, 1H, J = 11.9 Hz), 5.27 (ddd, 1H, J = 3.8, 3.8, 7.0 Hz), 5.81 (d, 1H, J = 7.0 Hz), 7.23−7.41 (m, 8H), 7.56 (d, 1H, J = 7.0 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.8, 34.2, 37.8, 63.4, 68.6, 78.9, 125.1, 127.1, 128.1, 128.2, 128.3, 128.4, 129.9, 135.3, 138.2, 139.2, 152.6, 160.7, 167.5; MS (EI) m/z (relative intensity, %) 378 (M^+, 10), 116 (39), 91 (100); HRMS (EI) calcd for $C_{21}H_{18}N_2O_5$ $(M)^+$ 378.1216, found 378.1213; $[\alpha]^{15}_D$ +260.3 (c 0.93, $CHCl_3$).

*(3aS-cis)-3-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-3,3a,8,8a-tetrahydro-2H-indeno[1,2-d]-2-oxazolidinone [**3e-(S,R,S)**] (major isomer).* Colorless solid (48.7 mg, 86%, 88:12); mp 46−47 °C; R_f = 0.20 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1701, 1734, 1776 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.61−2.63 (m, 2H), 3.40−3.42 (m, 2H), 4.53−4.56 (m, 1H), 5.12 (d, 1H, J = 12.3 Hz), 5.24 (d, 1H, J = 12.3 Hz), 5.35 (ddd, 1H, J = 3.0, 4.6, 7.3 Hz), 5.94 (d, 1H, J = 7.3 Hz), 7.13−7.38 (m, 8H), 7.52 (d, 1H, J = 7.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 32.7, 34.5, 38.0, 63.1, 68.5, 78.6, 124.9, 127.2, 128.1, 128.2, 128.3, 129.9, 135.1, 138.0, 139.0, 152.6, 160.7, 167.7; MS (EI) m/z (relative intensity, %) 378 (M^+, 9), 116 (50), 91 (100); HRMS (EI) calcd for $C_{21}H_{18}N_2O_5$ $(M)^+$ 378.1216, found 378.1213; $[\alpha]^{15}_D$ = +162.3 (c 1.00, $CHCl_3$).

*(4S)-3-[{(2′R)-(1′-Benzyloxycarbonyl-3′-ethoxycarbonyl)aziridin-2′-yl}carbonyl]-4-phenyl-2-oxazolidinone [**3f-(S,R)**] (major isomer).* Colorless oil (36.7 mg, 60%, 76:24); R_f = 0.30 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (neat) 1738, 1786 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.31 (t, 3H, J = 7.0 Hz), 1.45 (s, 9H), 3.27 (d, 1H, J = 2.2 Hz), 4.17−4.32 (m, 2H), 4.37 (dd, 1H, J = 3.2, 8.9 Hz), 4.71 (d, 1H, J = 2.2 Hz), 4.78 (dd, 1H, J = 8.6, 8.9 Hz), 5.43 (dd, 1H, J = 3.2, 8.6 Hz), 7.27−7.40 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 27.9, 39.7, 41.1, 57.8, 62.2, 70.6, 82.7, 125.9, 128.8, 129.1, 137.9, 153.1, 156.7, 164.7, 166.0; MS (CI, isobutane) m/z (relative intensity, %) 405 (M^+ + H, 1), 389 (2), 361 (2), 349 (12), 305 (100); HRMS (CI, isobutane) calcd for $C_{20}H_{25}N_2O_7$ $(M + H)^+$ 405.1662, found 405.1668; $[\alpha]^{15}_D$ = +39.2 (c 0.95, $CHCl_3$).

*(4S)-3-[{(2′S)-(1′-Benzyloxycarbonyl-3′-ethoxycarbonyl)aziridin-2′-yl}carbonyl]-4-phenyl-2-oxazolidinone [**3f-(S,S)**] (minor isomer).* Colorless solid (36.7 mg, 60%, 76:24); mp 50−51 °C; R_f = 0.20 (hexane/EtOAc, 6:4, v/v, silica gel plate); IR (KBr) 1738, 1786 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.31 (t, 3H, J = 7.0 Hz), 3.30 (d, 1H, J = 2.2 Hz), 4.19−4.32 (m, 2H), 4.39 (dd, 1H, J = 4.1, 8.9 Hz), 4.66 (d, 1H, J = 2.2 Hz), 4.77 (dd, 1H, J = 8.9, 8.9 Hz), 5.42 (dd, 1H, J = 4.1, 8.9 Hz), 7.30−7.39 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 27.5, 39.9, 41.3, 57.8, 62.1, 70.4, 82.5, 126.2, 128.8, 129.1, 137.7, 153.0, 156.7, 165.0, 166.0; MS (CI, isobutane) m/z (relative intensity, %) 405 (M^+ + H, 1), 389 (1), 361 (2), 349 (9), 305 (100); HRMS (CI, isobutane) calcd for $C_{20}H_{25}N_2O_7$ $(M + H)^+$ 405.1662, found 405.1656; $[\alpha]^{15}_D$ +107.5 (c 0.73, $CHCl_3$).

*(4R,7S)-1-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-7-isopropyl-4-methyl-3-phenyl-4,5,6,7-tetrahydro-1H-indazole [**3g-(R,S,S)**].* Colorless oil (33.4 mg, 75%, 95:5); R_f = 0.55 (hexane/EtOAc, 7:3, v/v, silica gel plate); IR (neat) 1734 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.87−0.97 (m, 9H), 1.45−1.51 (m, 1H), 1.70−1.80 (m, 2H), 2.03−2.12 (m, 2H), 2.63 (dd, 1H, J = 1.6, 5.7 Hz), 2.72 (dd, 1H, J = 1.6, 3.2 Hz), 3.15−3.25 (m, 1H), 3.27−3.35 (m, 1H), 4.78 (dd, 1H, J = 3.2, 5.7 Hz), 5.20 (s, 2H), 7.31−7.46 (m, 8H), 7.77−7.80 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.7, 19.9, 20.7, 21.1, 25.8, 26.9, 31.5, 32.7, 35.1, 37.8, 68.5, 125.4, 127.5, 128.2, 128.4, 128.5, 128.8, 132.6, 135.4, 146.3, 153.6, 161.1, 166.6; MS (EI) m/z (relative intensity, %) 457 (M^+, 3), 429 (4), 414 (1), 366 (13), 338 (15), 301 (19), 294 (13), 253 (21), 211 (25), 91 (100); HRMS (EI) calcd for $C_{28}H_{31}N_3O_3$ $(M)^+$ 457.2367, found 457.2373; $[\alpha]^{15}_D$ −14.6 (c 1.42, $CHCl_3$) (90% de).

*(4R,7S)-1-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-7-isopropyl-4-methyl-3-phenyl-4,5,6,7-tetrahydro-1H-indazole [**3h-(R,S,S)**].* Colorless oil (32.6 mg, 77%, >99:<1); R_f = 0.43 (hexane/EtOAc, 7:3, v/v, silica gel plate); IR (neat) 1732 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.85−1.02 (m, 9H), 1.46 (s, 9H), 1.75−1.83 (m, 2H), 2.02−2.20 (m, 2H), 2.56 (dd, 1H, J = 1.6, 5.7 Hz), 2.67 (dd, 1H, J = 1.6, 3.2 Hz), 3.20−3.30 (m, 1H), 3.34−3.39 (m, 1H), 4.67 (dd, 1H, J = 3.2, 5.7 Hz), 7.41−7.49 (m, 3H), 7.80−7.84 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.7, 19.9, 20.8, 21.1, 25.8, 27.0, 28.0, 31.5, 32.5, 35.2, 37.9, 81.9, 125.2, 127.5, 128.5, 128.7, 132.8, 146.2, 153.4, 159.9, 166.9; MS (EI) m/z (relative intensity, %) 423 (M^+, 3), 253 (58), 211 (100); HRMS (EI) calcd for $C_{25}H_{33}N_3O_3$ $(M)^+$ 423.2522, found 423.2524; $[\alpha]^{15}_D$ −24.2 (c 1.33, $CHCl_3$).

*(4S,7R)-1-[{(2′S)-(1′-Benzyloxycarbonyl)aziridin-2′-yl}carbonyl]-7-isopropyl-4-methyl-3-phenyl-4,5,6,7-tetrahydro-1H-indazole [**3h-(S,R,R)**].* Colorless oil (30.7 mg, 72%, >99:<1); R_f = 0.43 (hexane/EtOAc, 7:3, v/v, silica gel plate); IR (neat) 1730 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.85−1.02 (m, 9H), 1.46 (s, 9H), 1.75−1.83 (m, 2H), 2.02−2.20 (m, 2H), 2.56 (dd, 1H, J = 1.6, 5.7 Hz), 2.67 (dd, 1H, J = 1.6, 3.2 Hz), 3.20−3.30 (m, 1H), 3.34−3.39 (m, 1H), 4.67 (dd, 1H, J = 3.2, 5.7 Hz), 7.41−7.49 (m, 3H), 7.80−7.84 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.6, 19.8, 20.7, 21.0, 25.7, 26.9, 27.9, 31.4, 32.4, 35.1, 37.8, 81.8, 125.1, 127.4, 128.4, 128.6, 132.6, 146.1, 153.3, 159.8, 166.8; MS (EI) m/z (relative intensity, %) 423 (M^+, 3), 253 (56), 211 (100); HRMS (EI) calcd for $C_{25}H_{33}N_3O_3$ $(M)^+$ 423.2522, found 423.2519; $[\alpha]^{15}_D$ +23.9 (c 1.43, $CHCl_3$).

*(2S)-1-Benzyloxycarbonylaziridine-2-carboxylic Acid Methyl Ester [**3i-(S)**].* Colorless oil (16.1 mg, 78%); R_f = 0.49 (hexane/EtOAc, 1:1, v/v, silica gel plate); HPLC (Daicel Chiralcel OD, hexane/2-propanol, 9:1, 0.2 mL/min, 254 nm, 30 °C) t = 56.8 and 66.0 min.; IR (neat) 1732, 1743 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.49 (dd, 1H, J = 1.2,

5.4 Hz), 2.60 (dd, 1H, J = 1.2, 3.2 Hz), 3.11 (dd, 1H, J = 3.2, 5.4 Hz), 3.71 (s, 3H), 5.13 (d, 1H, J = 10.5 Hz), 5.17 (d, 1H, J = 10.5 Hz), 7.36 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 31.4, 34.9, 52.7, 68.6, 128.3, 128.4, 135.2, 160.5, 168.4; MS (CI, isobutane) m/z (relative intensity, %) 236 ($M^+ + H$, 20), 192 ($M^+ + H - CO_2$, 100), 91 (CH_2Ph, 39); HRMS (CI, isobutane) calcd for $C_{12}H_{14}NO_4$ $(M + H)^+$ 236.0923, found 236.0917; $[\alpha]^{15}_D$ −48.5 (c 1.00, $CHCl_3$).

Typical Procedure for the Preparation of Chiral 3-Acryloyl-2-oxazolidinones.[31] To the solution of acrylic acid (8.1 mmol) and triethylamine (16.5 mmol) in THF (23 mL) was added acryloyl chloride (7.2 mmol) at −20 °C. After the mixture was stirred at −20 °C for 1 h, lithium chloride (12.0 mmol) and chiral oxazolidinone (3 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by addition of 0.2 M HCl aq (20 mL), and THF was removed in vacuo. The residue was extracted with ethyl acetate (30 mL × 3). The organic layer was washed subsequently with saturated sodium bicarbonate (20 mL) and brine (20 mL). The organic solution was then dried over anhydrous magnesium sulfate and concentrated to give the crude product. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give the corresponding olefins.

Typical Procedure for the Preparation of *N*-Acryloyl-L-menthopyrazole.[32] *(2S,5R)-2-Isopropyl-5-methylcyclohexanone.*[33] Pyridinium chlorochromate (2.04 g, 10.5 mmol) and silica gel 60 (2.04 g, purchased from Nacalai Tesque Co., average diameter: 75 μm) was ground to a fine powder using a mortar and pestle. The light orange mixture was added to a round-bottom flask containing dichloromethane (21 mL). To the resulting suspension was added a solution of L-menthol (990 mg, 6.3 mmol) in dichloromethane (5 mL). After the mixture was stirred at room temperature for 5 h, the resulting suspension was diluted with diethyl ether (60 mL) and filtered at reduced pressure through a Büchner funnel layered with Celite and silica gel. The filtrate was concentrated and purified by Kugelrohr distillation to give the corresponding ketone (2.98 g, 92%). Spectroscopic data were in agreement with those of previously published material. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (d, 3H, J = 6.6 Hz), 0.91 (d, 3H, J = 6.6 Hz), 1.01 (d, 3H, J = 5.9 Hz), 1.32−1.42 (m, 2H), 1.77−1.93 (m, 2H), 1.95−2.18 (m, 4H), 2.36 (ddd, 1H, J = 2.2, 3.6, 12.7 Hz).

(3R, 6S)-2-Benzoyl-6-isopropyl-3-methylcyclohexanone.[34] L-Menthone (3.01 g, 19.5 mmol) was added to THF solution (21 mL) of lithium diisopropylamine (LDA) which was prepared in situ from diisopropylamine (2.90 g, 28.6 mmol) and *n*-butyllithium (20 mL, 1.65 M in hexane) at −78 °C. After the mixture was stirred for 30 min at −78 °C, it was treated with benzoyl chloride (3.30 g, 23.5 mmol) in THF (11 mL) and then warmed up to room temperature. After the mixture was stirred for 2 h at room temperature, it was quenched with 1 M hydrochloric acid and extracted with ether (20 mL × 5). The combined organic layer was washed subsequently with saturated sodium bicarbonate (20 mL) and brine (20 mL). The organic solution was then dried over anhydrous magnesium sulfate and concentrated to give the crude product. The residue was purified by recrystallization from hexane to give product (2.67 g, 89%). Spectroscopic data were in agreement with those of previously published material. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.86 (d, 3H, J = 6.8 Hz), 0.92 (d, 3H, J = 6.8 Hz), 0.98 (d, 3H, J = 6.5 Hz), 1.45−1.60 (m, 2H), 2.02−2.17 (m, 2H), 1.95−2.20 (m, 4H), 2.19−2.30 (m, 1H), 2.49−2.62 (m, 1H), 4.03 (d, 1H, J = 11.6 Hz), 7.41−7.57 (m, 3H), 7.81−7.84 (m, 2H).

3-Phenyl-(4R,7S)-4-methyl-7-isopropyl-4,5,6,7-tetrahydroindazole.[34] To a solution of (3*R*, 6*S*)-2-benzoyl-6-isopropyl-3-methylcyclohexanone (2.58 g, 10.0 mmol) in MeOH (24 mL) were added hydrazine hydrate (3.62 g, 72.0 mmol) and concd hydrochloric acid (350 μL). The mixture was refluxed for 16 h. The reaction mixture was cooled to room temperature and then acidified and extracted with dichloromethane (30 mL × 4). The combined organic layer was washed subsequently with sodium bicarbonate (30 mL) and brine (30 mL). The organic solution was then dried over anhydrous magnesium sulfate and concentrated to give the crude product. The residue was purified by silica gel column chromatography (hexane/ethyl acetate) to give product (2.38 g, 94%). Spectroscopic data were in agreement with those of previously published material. ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (d, 3H, J = 7.0), 1.00 (d, 3H, J = 7.0), 1.06 (d, 3H, J = 7.0), 1.25−1.38 (m, 1H), 1.52−1.65 (m, 1H), 1.81−1.90 (m, 1H), 2.00−2.10 (m, 1H), 2.18−2.32 (m, 1H), 2.62−2.69 (m, 1H), 3.05−3.12 (m, 1H), 7.30−7.44 (m, 3H), 7.58−7.61 (m, 2H).

(4R,7S)-1-Acryloyl-7-isopropyl-4-methyl-3-phenyl-4,5,6,7-tetrahydro-1H-indazole.[34] To the solution of 3-phenyl-L-menthopyrazole (251 mg, 0.98 mmol) in toluene (3 mL) were added triethylamine (297 mg, 2.9 mmol) and acryloyl chloride (270 mg, 2.9 mmol), and the mixture was stirred at room temperature for 2 h. The reaction was quenched with water and extracted with ether (20 mL x 4). The combined organic layer was washed subsequently with 1 M hydrochloric acid (20 mL) and brine (20 mL). The organic solution was then dried over anhydrous magnesium sulfate and concentrated to give the crude product. Regioisomers (**1g**-(*R*,*S*):**1g′**-(*R*,*S*) = 43:57) were separated by flash column chromatography on silica gel (hexane/toluene) to give the corresponding olefins (111 mg, 37%).

Preparation of Catalysts. Ammonium catalysts **CD1** and **CD2** are commercially available, and **CN1**,[35] **CN2**,[36] **CN3**,[37] and **CN4**[38] were prepared by following the procedures described in the literature.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) *Aziridines and Epoxides in Organic Synthesis*; Yudin, A. K., Ed.; Wiley-VCH: Weinheim, 2006.

(2) (a) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701–2743. (b) Lu, P. *Tetrahedron* **2010**, *66*, 2549–2560.

(3) (a) Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *J. Org. Chem.* **1990**, *55*, 4683–4681. (b) Åhman, J.; Jarevång, T.; Somfai, P. *J. Org. Chem.* **1996**, *61*, 8148–8159. (c) Åhman, J.; Somfai, P. *Tetrahedron* **1999**, *55*, 11595–11600. (d) Lindström, U. M.; Somfai, P. *Chem.—Eur. J.* **2001**, *7*, 94–98.

(4) (a) Lown, J. W. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 653−732. (b) Pinho e Melo, T. M. V. D. *Eur. J. Org. Chem.* **2006**, *13*, 2873. (c) Coldham, I.; Hufton, R. *Chem. Rev.* **2005**, *105*, 2765–2809.

(5) (a) Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1983**, *105*, 6731–6138. (b) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931–934.

(6) (a) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341–2372. (b) Osborn, H. M. I.; Sweeney, J. *Tetrahedron: Asymmetry* **1997**, *8*, 1693–1715. (c) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905–2919. (d) Katsuki, T. *Chem. Lett.* **2005**, *34*, 1304–1309. (e) Pellissier, H. *Tetrahedron* **2010**, *66*, 1509–1555.

(7) For aziridination of olefins, see: Shen, Y.-M.; Zhao, M.-X.; Xu, J.; Shi, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 8005-8008, and references therein.
(8) (a) Furukawa, N.; Yoshimura, T.; Ohtsu, M.; Akasaka, T.; Oae, S. *Tetrahedron* **1980**, *36*, 73–80. (b) Métra, P.; Hamelin, J. *J. Chem. Soc., Chem. Commun.* **1980**, 1038–1039. (c) Ikeda, I.; Machii, Y.; Okahara, M. *Synthesis* **1980**, 650–651. (d) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744–6746. (e) Pereira, M. M.; Santos, P. P. O.; Reis, L. V.; Lobo, A. M.; Prabhakar, S. *J. Chem. Soc., Chem. Commun.* **1993**, 38–40. (f) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753. (g) Fioravanti, S.; Pellacani, L.; Tabanella, S.; Tardella, P. A. *Tetrahedron* **1998**, *54*, 14105–14112. (h) Hori, K.; Sugihara, H.; Ito, Y. N.; Katsuki, T. *Tetrahedron Lett.* **1999**, *40*, 5207–5210. (i) Dauban, P.; Sanière, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7707–7708. (j) Siu, T.; Yudin, A. K. *J. Am. Chem. Soc.* **2002**, *124*, 530–531. (k) Colantoni, D.; Fioravanti, S.; Pellacani, L.; Tardella, P. A. *Org. Lett.* **2004**, *6*, 197–200. (l) Mahoney, J. M.; Smith, C. R.; Johnston, J. N. *J. Am. Chem. Soc.* **2005**, *127*, 1354–1355. (m) Fioravanti, S.; Colantoni, D.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **2005**, *70*, 3296–3298.
(9) Cardillo, G.; Gentilucci, L.; Tolomelli, A. *Aldrichim. Acta* **2003**, *36*, 39–50.
(10) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328–5329.
(11) (a) Aires-de-Sousa, J.; Lobo, A. M.; Prabhakar, S. *Tetrahedron Lett.* **1996**, *37*, 3183–3186. (b) Aires-de-Sousa, J.; Prabhakar, S.; Lobo, A. M.; Rosa, A. M.; Gomes, M. J. S.; Corvo, M. C.; Williams, D. J.; White, A. J. P. *Tetrahedron: Asymmetry* **2002**, *12*, 3349–3365. (c) Murugan, E.; Siva, A. *Synthesis* **2005**, 2022–2028.
(12) Armstrong, A.; Baxter, C. A.; Lamont, S. G.; Pape, A. R.; Wincewicz, R. *Org. Lett.* **2007**, *9*, 351–353.
(13) Vesely, J.; Ibrahem, I.; Zhao, G.-L.; Rios, R.; Córdova, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 778–781.
(14) Pesciaioli, F.; Vincentiis, F. D.; Galzerano, P.; Bencivenni, G.; Bartoli, G.; Mazzanti, A.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8703–8706.
(15) Minakata, S.; Murakami, Y.; Tsuruoka, R.; Kitanaka, S.; Komatsu, M. *Chem. Commun.* **2008**, 6363–6365.
(16) Gnas, Y.; Glorius, F. *Synthesis* **2006**, 1899–1930.
(17) (a) Fioravanti, S.; Morreale, A.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **2002**, *67*, 4972–4974. (b) Fioravanti, S.; Morreale, A.; Pellacani, L.; Tardella, P. A. *Eur. J. Org. Chem.* **2003**, 4549–4552. (c) Fioravanti, S.; Morreale, A.; Pellacani, L.; Tardella, P. A. *Tetrahedron Lett.* **2003**, *44*, 3031–3034.
(18) (a) Atkinson, R. S.; David, J. F.; Russell, R.; Tughan, G. *J. Chem. Soc., Chem. Commun.* **1986**, 832–834. (b) Atkinson, R. S.; Tughan, G. *J. Chem. Soc., Chem. Commun.* **1986**, 834–835. (c) Atkinson, R. S.; Tughan, G. *J. Chem. Soc., Perkin Trans 1*. **1987**, 2787–2796. (d) Atkinson, R. S.; Tughan, G. *J. Chem. Soc., Perkin Trans 1.* **1987**, 2797–2802. (e) Atkinson, R. S.; Tughan, G. J. *Chem. Soc., Perkin Trans 1* **1987**, 2803–2807. (f) Chilmonczyk, Z.; Egli, M.; Behringer, C.; Dreiding, A. S. *Helv. Chim. Acta* **1989**, *72*, 1095–1106. (g) Kapron, J. T.; Santarsiero, B. D.; Vederas, J. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1074–1076. (h) Garnet, P.; Dogan, O.; Pillai, S. *Tetrahedron Lett.* **1994**, *35*, 1653–1656. (i) Cardillo, G.; Gentilucci, L.; Tomasini, C.; Castejon-Bordas, M. P. V. *Tetrahedron: Asymmetry* **1996**, *7*, 755–762. (j) Cardillo, G.; Casolari, S.; Gentilucci, L.; Tomasini, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1848–1849. (k) Bongini, A.; Cardillo, G.; Gentilucci, L.; Tomasini, C. *J. Org. Chem.* **1997**, *62*, 9148–9153. (l) CardilloG.; Gentilucci, L.; Bastardas, I. R.; Tolomelli, A. *Tetrahedron* **1998**, *54*, 8217–8222. (m) Atkinson, R. S.; Barker, E.; Ulukanli, S. *J. Chem. Soc., Perkin Trans 1* **1998**, 583–589. (n) Atkinson, R. S.; Ulukanli, S. *J. Chem. Soc., Perkin Trans 2* **1999**, 771–776. (o) Yang, K.-S.; Chen, K. *J. Org. Chem.* **2001**, *66*, 1676–1679. (p) Ishihara, H.; Ito, Y. N.; Katsuki, T. *Chem. Lett.* **2001**, *30*, 984–985. (q) Atkinson, R. S.; Draycott, R. D.; Hirst, D. J.; Parratt, M. J.; Raynham, T. M. *Tetrahedron Lett.* **2002**, *43*, 2083–2085. (r) Ishihara, H.; Hori, K.; Sugihara, H.; Ito, Y. N.; Katsuki, T. *Helv. Chim. Acta* **2002**, *85*, 4272–4286. (s) Ulukanli, S.; Karabuga, S.; Celik, A.; Kazaz, C. *Tetrahedron Lett.* **2005**, *46*, 197–199. (t) Bew, S. P.; Hughes, D. L.; Savic, V.; Soapi, K. M.; Wilson, M. A. *Chem. Commun.* **2006**, 3513–3515. (u) Duan, P.-W.; Chiu, C.-C.; Lee, W.-D.; Pan, L. S.; Venkatesham, U.; Tzeng, Z.-H.; Chen, K. *Tetrahedron: Asymmetry* **2008**, *19*, 682–690.
(19) (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127–2129. (b) Evans, D. A. *Aldrichim. Acta* **1982**, *15*, 23–32.
(20) Ho, G.-J.; Mathre., D. J. *J. Org. Chem.* **1995**, *60*, 2271–2273.
(21) Although the reaction of crotonylated chiral oxazolidinone with chloramine salt **2a** afforded desired aziridine, chemical yield and diastereoselectivity were low (30% yield; dr = 1:1).
(22) (a) Kashima, C.; Fukuchi, I.; Takahashi, K.; Hosomi, A. *Tetrahedron Lett.* **1993**, *34*, 8305–8308. (b) Kashima, C. *Heterocycles* **2006**, *60*, 959–987.
(23) Although we examined enantioselective aziridination of achiral olefins using chloramine **2b**, no significant improvement in either reactivity or selectivity was observed. For example, the reaction of 3-acryloyloxazolidin-2-one with **2b** in the presence of chiral catalyst **CD2** in CH_2Cl_2 at room temperature for 2 h gave the corresponding chiral aziridine with (*S*)-configuration in 75% yield with 59% ee, whereas the reaction with **2a** under the same reaction conditions afforded the product in 98% yield with 63% ee.[15]
(24) (a) Corey, E. J.; Xu, F.; Noe, M. C. *J. Am. Chem. Soc.* **1997**, *119*, 12414–12415. (b) Corey, E. J.; Bo, Y.; Busch-Petersen, J. *J. Am. Chem. Soc.* **1998**, *120*, 13000–13001.
(25) Andrus, M. B.; Ye, Z.; Zhang, J. *Tetrahedron Lett.* **2005**, *46*, 3839–3842.
(26) Yang, K.-S.; Chen, K. *Org. Lett.* **2002**, *4*, 1107–1109.
(27) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238–1256.
(28) Sibi, M. P.; Soeta, T.; Jasperse, C. P. *Org. Lett.* **2009**, *11*, 5366–5369.
(29) Kise, N.; Mimura, R. *Tetrahedron: Asymmetry* **2007**, *18*, 988–993.
(30) Cannizzaro, C. E.; Ashley, J. A.; Janda, K. D.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 2489–2506.
(31) Ho, G.-J.; Mathre, D. J. *J. Org. Chem.* **1995**, *60*, 2271–2273.
(32) See the Supporting Information.
(33) Luzzio, F. A.; Fitch, R. W.; Moore, W. J.; Mudd, K. J. *J. Chem. Educ.* **1999**, *76*, 974–975.
(34) Kashima, C.; Fukuchi, I.; Hosomi, A. *J. Org. Chem.* **1994**, *59*, 7821–7824.
(35) Matsushita, M.; Yoshida, K.; Yamamoto, N.; Wirsching, P.; Lerner, R. A.; Janda, K. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5984–5987.
(36) O'Donnell, M. J.; Delgado, F.; Pottorf, R. S. *Tetrahedoron* **1999**, *55*, 6347–6362.
(37) Lygo, B.; Wainwright, P. G. *Tetrahedron* **1999**, *55*, 6289–6300.
(38) Kim, D. Y.; Park, E. J. *Org. Lett.* **2002**, *4*, 545–547.