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Reduction of 2-Acylaziridines by Samarium(II) Iodide. An Efficient and Regioselective Route to β-Amino Carbonyl Compounds.

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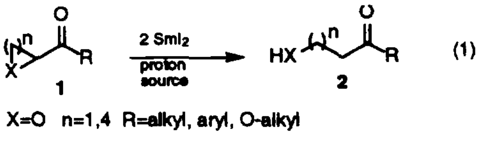
Dedicated with great respect and admiration to Professor Samuel Danishefsky on the occasion of his well-deserved receipt of the **Tetrahedron Prize** for 1996.

Abstract: A convenient method for the reduction of 2-acylaziridines, aziridine-2-carboxylates and aziridine-2-carboxamides is described. The reduction of all of the substrates examined was extremely rapid and highly regioselective, giving rise to β-amino carbonyl compounds. This method appears to be general for all of the classes of aziridines mentioned above, and also tolerates a variety of nitrogen protecting groups. © 1997 Elsevier Science Ltd.

INTRODUCTION

Samarium(II) iodide (SmI_2) is a powerful, one-electron reducing agent, capable of reducing a wide range of functional groups with a high degree of selectivity.[1] One of the most widely applied processes using SmI_2 involves the reductive cleavage of α-heterosubstituted carbonyl substrates.[1] Substrates possessing small rings adjacent to a carbonyl group comprise an important subgroup of compounds that can be reductively cleaved. Epoxy ketones[2] and -esters,[3] vinyl epoxides,[4] vinylogous epoxides,[5] and cyclopropyl ketones[6] and -esters[7] have been reduced with SmI_2 to provide the corresponding ring-opened products (eq 1). Tetrahydropyrans bearing an α-ketone have also been reduced to afford the ring-opened hydroxy ketones, indicating that this type of reduction is not limited to small ring compounds.[8]



(1)

Noticeably absent from this list of substrates are those containing nitrogen heterocycles. To fill this void, a study was undertaken to determine if nitrogen substituents could serve as adequate leaving groups in the reductive cleavage process.[9] This ring scission would provide a novel method for the preparation of β-amino carbonyl compounds, intermediates that are important for the synthesis of biologically active compounds.

Over the last several years, numerous complementary methods for the synthesis of β-amino carbonyl compounds have been developed. β-Amino esters and -acids have received considerable attention and strategies used for their preparation are outlined in two excellent reviews.[10] Methods for the preparation β-amino ketones and aldehydes, particularly in enantiomerically pure form, are more limited.[11] Nucleophilic ring opening of aziridine-2-carboxylate esters has been a common strategy used for the synthesis of α- and β-amino acids. It is well known that heteronucleophiles attack the β-carbon giving rise to α-amino acids.[12] With the exception of nucleophilic Wittig reagents[13] and indoles,[14] which attack regioselectively at the β-carbon, carbon nucleophiles generally attack in a non-regioselective manner.[15] An additional problem with carbon nucleophiles is that the ester functionality is also subject to nucleophilic attack, thereby limiting this method further. Hydrolysis of the ester to the corresponding acid has been shown to correct this problem, and gives rise to regioselective attack at the β-carbon of the aziridine.[16]

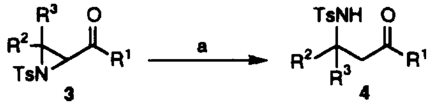
α- and β-Amino carbonyl compounds have also been prepared by the reductive ring opening of various acyl aziridines using a variety of reductants.[17] Either α- or β-amino carbonyl compounds can be prepared depending on the nature of the nitrogen protecting group and the substituents on the aziridine ring, but in general these methods have not been rigorously examined to determine their scope and limitations. Herein are reported successful attempts to synthesize β-amino carbonyl compounds selectively by employing SmI_2 as the reductant.

RESULTS AND DISCUSSION

Initially, a series of 2-acyl-*N*-tosyl aziridines was prepared for study. These were readily available from the $Cu(acac)_2$- or $Cu(CH_3CN)_4ClO_4$-catalyzed aziridination of α,β-unsaturated ketones using (*N*-(*p*-toluenesulfonyl)imino)phenyliodinane (PhI=NTs).[18] The *N*-tosyl aziridines were obtained in yields that varied from 21% (**3d**) to 56% (**3a**). Despite the low to moderate yields obtained, the simplicity of this one-step protocol was advantageous for preliminary studies. Treatment of **3a** with 2.5 equiv of SmI_2 in THF-MeOH solvent at -90 °C[2] provided the β-*N*-tosylamino ketone in an 87% yield. The reduction was extremely rapid. Thin layer chromatographic analysis indicated the complete consumption of the aziridine immediately after addition of the SmI_2. During the course of optimization experiments, varying amounts of over-reduced amino alcohols were obtained at higher temperatures. At room temperature, a substantial amount of heat was generated during the course of the reaction. The optimum conditions for the reduction of these 2-acylaziridines employed 2.05 equiv of SmI_2 in THF-MeOH solvent at 0 °C. This procedure was the simplest to carry out experimentally, and also provided control for the exothermicity of the reaction and led to high yields of isolated products. As shown in Table 1, the β-*N*-tosylamino ketones were obtained in excellent yields with no sign of desulfonylation.[19]

Next, the efficacy of this reductive cleavage with *N*-tosylaziridine-2-carboxylates was examined. Again, these compounds were prepared via the copper catalyzed aziridination[17b,18] in yields ranging from 18-38%. Enantiomerically pure aziridine **5d**[20] was prepared from L-threonine using known methods.[21]

Table 1. Reduction of 2-Acyl Aziridines with SmI_2

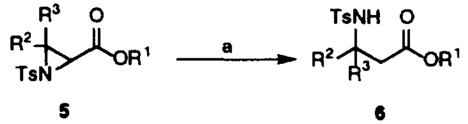


aziridine	product (% yield)
3a R^1= Me; R^2 = H; R^3= Ph	**4a** (82)
3b R^1= Me; R^2, R^3 = H	**4b** (79)
3c R^1= Me; R^2,R^3= Me	**4c** (88)
3d R^1, R^2= $(CH_2)_3$; R^3 = H	**4d** (82)

a. 2.05 equiv SmI_2, MeOH, THF, 0 °C

At the outset, treatment of aziridine **5a** with 2.5 equiv of SmI_2 in THF-EtOH solvent at 0 °C provided a mixture of α- and β-amino esters. The use of *N*,*N*-dimethylethanolamine (DMEA) as an additive was explored in an effort to rectify this problem.[3a] The reduction of esters by electron transfer agents is more difficult than that of ketones, and in initial investigations it appeared that Sm(III) Lewis acid-promoted ring opening of the aziridine was competing with the reductive mode of ring cleavage, thus leading to poor regioselectivity. DMEA is believed to serve several roles in these reductions. Not only does it serve as an effective proton source, but it also is an efficient chelator of the Lewis acidic Sm(III) species in the reaction mixture.[3a] Additionally, it may increase the reduction potential of the Sm(II) reductant, thereby allowing the exclusive formation of a ketyl. This could be important in reactions where reductive processes are competing with Lewis acid-promoted side reactions. Through these effects, DMEA prevents the regioselectivity problem observed in its absence. Thus, as was the case for epoxy esters,[3a] performing the reductions in the presence of 5.0 equiv of DMEA in place of methanol or ethanol provided exclusively the desired β-amino esters in excellent yields (Table 2). Of additional note, aziridine **5d** was cleanly reduced to give the desired product **6d** in 86% yield in greater than 95% ee as determined by Eu^{3+} shift studies.

Table 2. Reduction of *N*-Ts Aziridine-2-Carboxylates with SmI_2



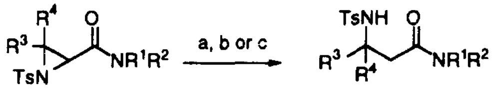
aziridine	product (% yield)
5a R^1=Et; R^2 = H R^3=Ph	**6a** (87)
5b R^1=Et; R^2, R^3 = H	**6b** (98)
5c R^1,R^2,R^3=Me	**6c** (87)
5d R^1,R^3=Me; R^2 = H	**6d** (86, >95% ee)

a. 2.5 equiv SmI_2, 5.0 equiv DMEA, THF, 0 °C

To complete the study of acyl group compatibility with this reductive process, a series of *N*-tosyl aziridine-2-carboxamides was prepared. Aziridine **7a** was prepared via the copper-catalyzed aziridination in excellent yield, while the aziridine **7c** was obtained in moderate yield by the same procedure. The remaining substrates were prepared from the corresponding NH aziridines, which were made using known methods.[22,23]

With these substrates in hand, they were subjected to SmI_2 treatment in the presence of DMEA. Initially the reductions were performed using the conditions described previously for aziridine-2-carboxylate esters. Under these conditions, the corresponding β-amino amides were obtained in 50-60% yields. Varying amounts of *p*-toluenesulfonamide were observed in the crude ^1H NMR, thereby accounting for the modest yields. Additionally, as these β-amino amides are very polar compounds, extraction from the aqueous quench proved difficult. Ultimately, it was found that the yields were improved when the reactions were performed at -25 °C and quenched with an aqueous solution of 20% sodium potassium tartrate (Rochelle's salt) in place of the basic sodium bicarbonate solution.[24] As an additional measure, chromatographic purification was performed using neutral (pH 7) silica gel. This protocol provided the desired products **8a** and **8b** in 86% and 70% yields respectively (Table 3).

Table 3. Reduction of *N*-Ts Aziridine-2-Carboxamides with SmI_2



7 **8**

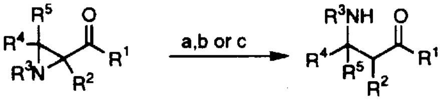
aziridine	product (% yield)
7a R^1,R^2=Me; R^3, R^4 = H	**8a** (86)^a
7b R^1,R^2=Et; R^3=Me; R^4 = H	**8b** (70)^a
7c R^1=Me; R^2=OMe; R^3, R^4 = H	**8c** (70)^b
7d R^1,R^3=Me; R^2=OMe; R^4 = H	**8d** (70)^b
7d R^1,R^3=Me; R^2=OMe; R^4 = H	**8e** (73 R^2=H)^c
7e R^1,R^3,R^4=Me; R^2=OMe	**7f** (60 R^2=H)^b

a. 2.5 equiv SmI_2, 5.0 equiv DMEA, THF, -25 °C b. 2.05 equiv SmI_2, 5.0 equiv DMEA, THF, -40 °C c. 5.1 equiv SmI_2, 10.0 equiv DMEA, THF, 0 °C

The *N*-methoxy-*N*-methyl aziridine-2-carboxamides proved to be more problematic. For example, treatment of **7c** with 2.5 equiv SmI_2 and 5.0 equiv of DMEA in THF at 0 °C provided the desired product **8c** in only 51% yield accompanied with a 19% yield of *N*-methyl-3-(*p*-toluenesulfonamido)propanamide, where the N-O bond of the *N*-methoxy group had been reduced.[25] Reducing the amount of SmI_2 to 2.05 equiv increased the ratio of **8c**:*N*-methyl-3-(*p*-toluenesulfonamido)propanamide to 6:1, but did not eliminate the over-reduction. Ultimately, performing the reductions at -40 °C with 2.05 equiv SmI_2 eliminated the formation of *N*-methyl-3-(*p*-toluenesulfonamido)propanamide and provided **8c** in 70% yield (Table 3). Surprisingly, reduction of **7e** using these optimized conditions provided **7f** in 60% yield. In this case, N-O bond cleavage occurred preferentially to C-N bond cleavage. Lastly, treatment of **7d** with 5.0 equiv SmI_2 and 10.0 equiv of DMEA in THF at 0 °C provided the completely reduced product **8e** in 73% yield.

To establish the generality of this method, the compatibility of this reductive cleavage with other nitrogen protecting groups was examined. To this end, several N-H aziridine-2-carboxylate esters were prepared from the corresponding epoxides using known methods.[23] With these aziridines in hand, a variety of common nitrogen protecting groups was introduced in a straightforward manner. Treatment of these substrates with 2.5 equiv of SmI_2 and 5.0 equiv of DMEA in THF at 0 °C provided the β-amino esters in good to excellent yields (Table 4). Reduction of **9e** and **9f** demonstrates an inherent limitation to this method, in that stereochemistry adjacent to the carbonyl cannot be reliably controlled. Thus, 2.5:1 and 1.8:1 mixtures of diastereomers, respectively, were obtained upon aqueous workup of the reactions. As can be seen, this reductive cleavage is tolerant of a variety of nitrogen protecting groups. The successful reduction of **9g** demonstrates that an electron-withdrawing group on nitrogen is not required for the ring scission. Even unprotected aziridines were successfully reduced to provide moderate yields of β-amino esters. Reduction of **9h** provided a 28% yield of **10h** accompanied by a 16% yield of *N*-benzyl glycine ethyl ester, resulting from the cleavage of the C-C bond of the aziridine. This mode of cleavage has been observed with aryl or vinyl substituted epoxides.[26] Reduction of **9i** provided the desired product **10i** in 66% as the only isolable product, further supporting the directing effect of the aryl substituent on the previously observed C-C bond cleavage.

Table 4. Nitrogen Protecting Group Compatability



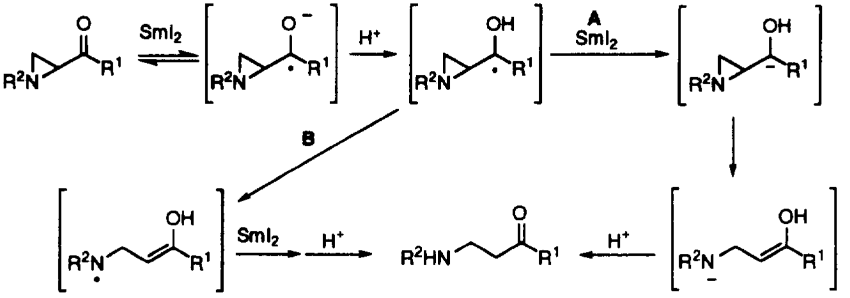
9 **10**

aziridine	product (% yield)
9a R^1=OEt; R^3=Ac; R^5=Ph; R^2, R^4 = H	**10a** (89)[a]
9b R^1=OEt; R^3=Boc; R^5=Ph; R^2, R^4 = H	**10b** (82)[a]
9c R^1=OMe; R^3=Boc; R^4=$Ph(CH_2)_2$; R^2, R^5 = H	**10c** (98)[a]
9d R^1=OMe; R^3=Fmoc; R^4=$Ph(CH_2)_2$; R^2, R^5 = H	**10d** (91)[a]
9e R^1=OMe; R^3=Ac; R^2,R^4=$(CH_2)_4$; R^5 = H	**10e** (72)[a,d]
9f R^1=Me; R^3=CO_2Et; R^2,R^4 =$(CH_2)_4$; R^5 = H	**10f** (69)[a,e]
9g R^1=OMe; R^3=Tr; R^2, R^4, R^5 = H	**10g** (82)[a]
9h R^1=OMe; R^4=Ph; R^2, R^3, R^5=H	**10h** (28)[a,f]
9i R^1=OMe; R^4=$Ph(CH_2)_2$; R^2, R^3, R^5=H	**10i** (66)[a]
9j R^1=Me; R^3=Boc; R^4=Me; R^2, R^5 = H	**10j** (92)[b]
9k R^1=Me; R^3=Boc; R^4=$Ph(CH_2)_2$; R^2, R^5 = H	**10k** (97)[b]
9l R^1=Ph; R^3=Boc; R^4=$Ph(CH_2)_2$; R^2, R^5 = H	**10l** (82)[c]

a. 2.5 equiv SmI_2, 5.0 equiv DMEA, THF, 0 °C b. 2.5 equiv SmI_2, 5.0 equiv DMEA, THF, 0 °C c. 2.5 equiv SmI_2, 5.0 equiv DMEA, THF, 0 °C d. 1.8:1 cis:trans e. 2.5:1 trans:cis f. 16% *N*-Bn glycine Me ester obtained as a side product.

A mechanistic rationale for the process is displayed in Scheme 1. Reaction of SmI_2 with the carbonyl generates a ketyl, which is rapidly protonated by the proton source. At this stage cleavage of the aziridine could occur by two distinct pathways. The protonated ketyl could undergo further reduction by the second equivalent of SmI_2, producing a carbanion. This anion would then induce the ring-opening of the aziridine (pathway A). Tautomerization of the intermediate enol would provide the observed β-amino carbonyl, with loss of stereochemistry adjacent to the carbonyl. Perhaps a more plausible mechanistic interpretation involves a radical ring scission, producing the nitrogen radical (pathway B). Further reduction of the nitrogen radical to a nitrogen anion by the second equivalent of SmI_2 followed by protonation would lead to the observed products.

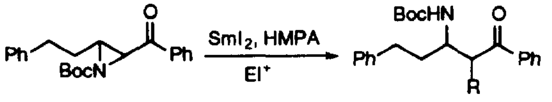
Scheme 1. Mechanistic Rationale



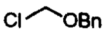
In light of this mechanistic interpretation, in the absence of a proton source this ring scission should provide an enolate anion that could be useful in forming new carbon-carbon bonds. This transformation would be particularly effectual if bond formation occurred with a high degree of diastereoselectivity. A brief study was undertaken to determine the scope of this process. At the outset, the reductive ring scission/alkylation sequence was examined with aziridine-2-carboxylate esters. Diastereoselective alkylation of the β-amino ester enolate intermediate would provide a versatile route to substituted β-amino esters and -acids. Initially, attempts were made to reproduce the reduction of **9c** in the absence of a proton source. Treatment of **9c** with 2.5 equiv of SmI_2 in THF at 0 °C resulted in the recovery of the starting material. Adding hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), or *N,N,N',N'*-tetramethylethylenediamine (TMEDA), additives that are known to increase the reduction potential of SmI_2, indeed resulted in the consumption of the starting material. Unfortunately, complex mixtures were obtained. Realizing that the ester enolate may be too unstable for subsequent protonation, the reduction/alkylation sequence was attempted. Treatment of **9c** with 2.5 equiv of SmI_2 and 5.0 equiv of HMPA in THF in the presence of 4.0 equiv of iodomethane also resulted in the formation of complex mixtures. Adding iodomethane subsequent to SmI_2 treatment did not improve the outcome.

Next, the reduction/alkylation of methyl ketone **9k** was examined. Unfortunately, attempts to alkylate the ketone enolate intermediate with iodomethane or benzyl bromide at 0 °C and -78 °C failed. Attention then turned to phenyl ketone **9l**, with the expectation that the added conjugation would provide stability to the enolate intermediate.[8] Again, attempts to quench the Sm(III) enolate with iodomethane or chloromethyl benzyl ether at low temperatures failed. However, alkylation with benzyl bromide and allyl bromide at -78 °C provided the substituted ketones **11a** and **11b** in moderate yields as mixtures of diastereomers (Table 5). With such restrictions, this sequence would be of limited utility. Although not examined in the present case, it may be possible that such alkylations can be achieved utilizing excess lithium chloride as an additive in a procedure analogous to that reported by Link and Overman.[27]

Table 5. Alkylation of 2-Acyl Aziridines Following Reductive Cleavage

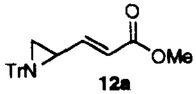
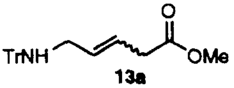
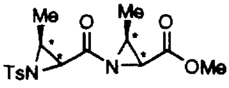
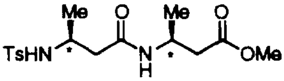
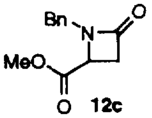
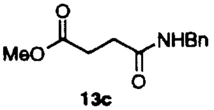


9l → **11**

El+	(R, % isoltd yield, ds)
MeI	—
	—
BnBr	**11a** (Bn, 62, 4.7 : 1)
	**11b** (allyl, 51, 5.2 : 1)

Several other classes of related compounds were treated with SmI_2/DMEA in THF in order to extend the scope of the reductive cleavage. For example, alkenylaziridine **12a**, obtained by reduction of **9g** to the aziridin-2-ylmethanol and subsequent oxidation to the aldehyde followed by Wittig chain extension, was treated with 2.5 equiv of SmI_2 and 5.0 equiv of DMEA in THF at 0 °C to provide a 2:1 mixture of olefinic isomers of the desired δ-amino pentenoate **13a** in excellent yield (Table 6). Bis-aziridine **12b**, readily prepared by amide bond formation using standard DCC coupling techniques, was treated with 5.0 equiv of SmI_2 and 10.0 equiv of DMEA in THF at 0 °C to provide the β-amino amide ester **13b** as a single diastereomer in excellent yield, thereby comprising a novel method for the preparation of β-amino amides.

Table 6. Extensions of the Method to Diverse Substrates

Substrate	Conditions	Product	Yield (%)
 **12a**	a	 **13a**	88 (2 : 1 E/Z)
 **12b**	b	 **13b**	86
 **12c**	c	 **13c**	72

a. 2.5 equiv SmI_2, 5.0 equiv DMEA, THF, 0 °C b. 5.0 equiv SmI_2, 10.0 equiv DMEA, THF, 0 °C c. 3.1 equiv SmI_2, 6.2 equiv DMEA, THF, 0 °C

Finally, azetidinones can be reductively cleaved as well, further extending the scope of this reaction. For example, azetidinone **12c**[28] was treated with 3.1 equiv of SmI_2 and 6.2 equiv of DMEA in THF at 0 °C to provide the ring opened product **13c** in 72% yield accompanied by a 27% yield of *N*-benzyl acetamide.

CONCLUSIONS

A convenient method for the reduction of 2-acylaziridines and aziridine-2-carboxylate esters and -amides has been developed. The reduction of all of the substrates examined was highly regioselective, giving rise to β-amino carbonyl compounds, one case in high enantiomeric purity. This method appears to be general for the classes of aziridines mentioned above and it also tolerates a variety of nitrogen protecting groups (Ts, RO_2C, Ac, Tr, Fmoc, H). Unfortunately, performing the reductions in the absence of a proton source in order to functionalize the enolate intermediates has not proven successful to this point. In spite of this apparent limitation, the reductive ring cleavage of aziridines with SmI_2 should prove highly useful in organic synthesis, and further development and extensions of the method are currently being explored.

EXPERIMENTAL SECTION

Reagents. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under Ar and then redistilled from sodium-benzophenone ketyl immediately prior to use. Samarium metal was purchased from Cerac, Inc. and stored under Ar. Diiodomethane (CH_2I_2) was purchased from Aldrich and was distilled prior to use. All solvents were distilled prior to use. Commercially available reagents were used with no further purification. Standard benchtop techniques were employed for handling air-sensitive reagents, and all reactions were performed under Ar. All intermediates leading up to the reductive cleavage step were prepared using literature procedures on readily available materials, and were judged to by >97% pure in each case by a combination of ^1H and ^{13}C NMR. They were carried on to the key intermediates for subjection to SmI_2 reductive cleavage.

General procedure for the formation of *N*-Tosylaziridines. To a 23 °C suspension of PhI=NTs[18a] (1.0 mmol) and the α,β-unsaturated carbonyl compound (2.0-5.0 mmol) in dry CH_3CN (12.5 mL) was added $Cu(acac)_2$ or $Cu(CH_3CN)_4ClO_4$ (8-10 mol %). Stirring under Ar proceeded until the reaction mixture was homogeneous, at which time it was filtered through a pad of silica gel and washed copiously with EtOAc. The filtrate was concentrated *in vacuo* to give an oil that was purified by flash column chromatography.

***trans*-2-Acetyl-3-phenyl-1-(*p*-toluenesulfonyl)aziridine (3a)**. The general procedure above was followed using PhI=NTs (200 mg, 0.53 mmol), $Cu(acac)_2$ (11 mg, 0.043 mmol), and *trans*-4-phenyl-3-buten-2-one (392 mg, 2.68 mmol). Reaction time: 1.67 h at 23 °C. Flash column chromatography (4:1 hexanes/EtOAc) provided 93.7 mg (56%) of the title compound: ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.39 (s, 3H), 3.71 (d, J = 4.2 Hz, 1H), 4.25 (d, J = 4.2 Hz, 1H), 7.23-7.31 (m, 7H), 7.68-7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 28.4, 48.5, 50.9, 127.3, 127.9, 128.3, 128.9, 129.5, 131.5, 136.4, 144.3, 200.3.

2-Acetyl-1-(*p*-toluenesulfonyl)aziridine (3b). The general procedure above was followed using PhI=NTs (600 mg, 1.61 mmol), $Cu(acac)_2$ (34 mg, 0.13 mmol), and methyl vinyl ketone (564 mg, 8.05 mmol). Reaction time: 2 h at 23 °C. Flash column chromatography (3:1 hexanes/EtOAc, then 2:1 hexanes/EtOAc) provided 172 mg (45%) of the title compound: mp 69-70.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.44 (s, 3H), 2.47 (d, J = 4.1 Hz, 1H), 2.78 (d, J = 7.4 Hz, 1H), 3.26 (dd, J = 7.4, 4.1 Hz, 1H), 7.34-7.36 (m, 2H), 7.80-7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 25.9, 31.8, 42.0, 128.2, 129.9, 133.9, 145.4, 201.4.

2-Acetyl-3,3-dimethyl-1-(*p*-toluenesulfonyl)aziridine (3c). The general procedure above was followed using PhI=NTs (800 mg, 2.14 mmol), $Cu(acac)_2$ (55 mg, 0.21 mmol), and 4-methyl-3-buten-2-one (1.05 g, 10.72 mmol). Reaction time: 12 h at 23 °C. Flash column chromatography (3:1 hexanes/EtOAc) provided 189 mg (33%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 3H), 1.79 (s, 3H), 1.94 (s, 3H), 2.41 (s, 3H), 3.45 (s, 1H), 7.30-7.32 (m, 2H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 21.8, 28.6, 53.2, 55.1, 127.3, 129.6, 137.2, 144.3, 202.0.

***cis*-2-Oxo-7-(*p*-toluenesulfonyl)-7-azabicyclo[4.1.0]heptane (3d).** The general procedure above was followed using PhI=NTs (600 mg, 1.61 mmol), $Cu(CH_3CN)_4ClO_4$ (32 mg, 0.13 mmol), and cyclohexenone (310 mg, 3.22 mmol). Reaction time: 0.5 h at 23 °C. Flash column chromatography (2:1 hexanes/EtOAc) provided 90 mg (21%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62-1.68 (m, 1H), 1.79-1.92 (m, 2H), 1.96-2.05 (m, 1H), 2.14-2.19 (m, 1H), 2.37-2.43 (m, 1H), 2.43 (s, 3H), 3.12 (d, J = 6.5 Hz, 1H), 3.43-3.45 (m, 1H), 7.32-7.34 (m, 2H), 7.78-7.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9, 21.5, 21.6, 36.9, 40.9, 43.7, 127.8, 129.8, 134.2, 145.0, 201.3.

Ethyl *trans*-3-Phenyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxylate (5a). The general procedure above was followed using PhI=NTs (400 mg, 1.07 mmol), $Cu(acac)_2$ (22 mg, 0.09 mmol), and ethyl cinnamate (944 mg, 5.36 mmol). Reaction time: 12 h at 23 °C. Flash column chromatography (4:1 hexanes/EtOAc) provided 188 mg (51%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 2.40 (s, 3H), 3.50 (d, J = 3.9 Hz, 1H), 4.26-4.34 (m, 2H), 4.42 (d, J = 3.9 Hz, 1H), 7.21-7.31 (m, 7H), 7.75-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.5, 47.0, 47.6, 62.3, 127.2, 127.4, 128.5, 128.8, 129.4, 132.6, 137.1, 144.2, 165.6.

Ethyl 1-(*p*-Toluenesulfonyl)aziridine-2-carboxylate (5b). The general procedure above was followed using PhI=NTs (800 mg, 2.14 mmol), $Cu(acac)_2$ (44 mg, 0.18 mmol), and ethyl acrylate (1.07 g, 10.72 mmol). Reaction time: 12 h at 23 °C. Flash column chromatography (3:1 hexanes/EtOAc) provided 218 mg (21%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1 Hz, 3H), 2.43 (s, 3H), 2.53 (d, J = 4.1 Hz, 1H), 2.73 (d, J = 7.1 Hz, 1H), 3.30 (dd, J = 7.1, 4.1 Hz, 1H), 4.12-4.20 (m, 2H), 7.32-7.35 (m, 2H), 7.81-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 21.4, 31.8, 35.6, 61.8, 127.9, 129.6, 133.7, 145.0, 166.5.

Methyl 3,3-Dimethyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxylate (5c). The general procedure above was followed using PhI=NTs (800 mg, 2.14 mmol), $Cu(CH_3CN)_4ClO_4$ (52 mg, 0.21 mmol), and methyl 3,3-dimethylacrylate (1.22 g, 10.72 mmol). Reaction time: 12 h at 23 °C. Flash column chromatography (4:1 hexanes/EtOAc) provided 229 mg (38%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.80 (s, 3H), 2.41 (s, 3H), 3.48 (s, 1H), 3.67 (s, 3H), 7.28-7.30 (m, 2H), 7.81-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.3, 21.5, 48.7, 52.2, 52.3, 127.2, 129.5, 137.2, 144.1, 166.7.

***N*,*N*-Dimethyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxamide (7a).** The general procedure above was followed using PhI=NTs (500 mg, 1.34 mmol), $Cu(CH_3CN)_4ClO_4$ (33 mg, 0.13 mmol), and *N*,*N*-dimethylacrylamide (664 mg, 6.70 mmol). Reaction time: 0.5 h at 23 °C. Flash column chromatography (2:1 hexanes/EtOAc, then 1:1 hexanes/EtOAc) provided 314 mg (87%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.62 (d, J = 6.9 Hz, 1H), 2.66 (d, J = 4.2 Hz, 1H), 2.96 (s, 3H), 3.21 (s, 3H), 3.57

(dd, J = 6.9, 4.2 Hz, 1H), 7.31-7.34 (m, 2H), 7.82-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 32.3, 35.1, 35.9, 37.1, 128.0, 129.7, 134.1, 145.0, 164.8.

N-Methoxy-N-methyl-1-(p-toluenesulfonyl)aziridine-2-carboxamide (7c). The general procedure above was followed using PhI=NTs (300 mg, 0.80 mmol), $Cu(CH_3CN)_4ClO_4$ (20 mg, 0.08 mmol), and N-methoxy-N-methylacrylamide (278 mg, 2.41 mmol). Reaction time: 12 h at 23 °C. Flash column chromatography (1.5:1 hexanes/EtOAc, then 1:1 hexanes/EtOAc) provided 82.4 mg (36%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.61 (d, J = 4.2 Hz, 1H), 2.66 (d, J = 6.9 Hz, 1H), 3.19 (s, 3H), 3.76 (s, 3H), 3.88 (dd, J = 6.7, 4.2 Hz, 1H), 7.29-7.32 (m, 2H), 7.80-7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 31.8, 32.4, 33.0, 62.1, 128.1, 129.7, 134.2, 145.0, 165.6.

Methyl (2S, 3S)-3-Methyl-1-(p-toluenesulfonyl)aziridine-2-carboxylate (5d). To a 0 °C solution of N-(p-toluenesulfonyl)threonine methyl ester (2.0 g, 6.96 mmol) in THF (125 mL) was added triphenylphosphine (2.74 g, 10.4 mmol) and diisopropylazodicarboxylate (DIAD) (2.11 g, 10.4 mmol). The resulting yellow solution was stirred for 1 h at 0 °C, then concentrated on a rotary evaporator. The residue was preadsorbed onto silica gel and then purified by flash column chromatography (3:1 hexanes/EtOAc) to provide 1.58 g (85%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (d, J = 5.8 Hz, 3H), 2.43 (s, 3H), 3.08 (dq, J = 7.5, 5.8 Hz, 1H), 3.36 (d, J = 7.5 Hz, 1H), 3.71 (s, 3H), 7.32-7.34 (m, 2H), 7.81-7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1, 21.6, 40.0, 52.6, 127.9, 129.8, 134.2, 145.0, 166.2.

General Procedure for the Preparation of N-H Aziridines. To a solution of epoxide (1.0 mmol) in $EtOH/H_2O$ (1.5:1, 0.1 M) was added ammonium chloride (2.0 mmol) and sodium azide (3.0 mmol). The resulting solution was heated to 65 °C for 16 h. The reaction mixture was cooled to 23 °C and concentrated. The aqueous residue was washed with $CHCl_3$ (3 x 20 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated. The crude residue was dissolved in CH_3CN (0.17 M) and triphenylphosphine (1.5 mmol) was added. The resulting solution was stirred at room temperature for 40 min, then heated to 80 °C for 12 h. The reaction mixture was cooled to room temperature and concentrated.

Ethyl *trans*-3-Phenyl-1H-aziridine-2-carboxylate (9h). Ethyl 3-phenyl glycidate (5.0 g, 26 mmol) was treated to the two-step procedure described above. Flash column chromatography (4:1 hexanes/EtOAc) provided 3.22 g (80% over two steps) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, J = 7.2 Hz, 3H), 1.88 (t, J = 8.5 Hz, 1H), 2.55 (dd, J = 8.0, 2.3 Hz, 1H), 3.23 (dd, J = 9.5, 2.3 Hz, 1H), 7.23-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 39.3, 40.1, 61.5, 125.9, 127.5, 128.2, 137.7, 171.5.

Methyl *trans*-3-(2-Phenylethyl)-1H-aziridine-2-carboxylate (9i). Methyl 3-(2-phenylethyl)oxirane-2-carboxylate[29] (3.82 g, 18.5 mmol) was treated to the two-step procedure described above. Flash chromatography (1.5:1 hexanes/EtOAc) provided 3.12 g (86%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 1H), 1.66-1.82 (m, 2H), 2.22-2.26 (m, 1H), 2.27 (d, J = 2.5 Hz, 1H), 2.67-2.83 (m, 2H), 3.73 (s, 3H), 7.14-7.19 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.1, 34.3, 35.0, 38.9, 52.2, 125.8, 128.2, 128.3, 140.9, 172.9.

***trans*-N-Methoxy-N-methyl-3-methyl-1H-aziridine-2-carboxamide (I).** *trans*-N-Methoxy-N-methyl-3-methyloxirane-2-carboxamide[30] (2.98 g, 20.0 mmol) was treated to the two-step procedure described above. Flash chromatography (2:1 EtOAc/hexanes, then 60:1 EtOAc/MeOH) provided 1.52 g (68%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, J = 5.5 Hz, 3H), 1.90-2.10 (s, 1H), 2.16-2.18 (m, 1H), 2.74 (s, 1H), 3.22 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 32.3, 33.9, 61.5, 171.2.

***N*-Methoxy-*N*-methyl-3,3-dimethyl-1H-aziridine-2-carboxamide (II).** *N*-Methoxy-*N*-methyl-3,3-dimethyloxirane-2-carboxamide[28] (2.51 g, 17.5 mmol) was treated to the two-step procedure described above. The reaction time for both steps was 48 h. Flash chromatography (15:1 EtOAc/MeOH) provided 1.17 g (53%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 3H), 1.29 (s, 3H), 1.54 (s, 1H), 2.79 (s, 1H), 3.23 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 25.5, 32.3, 38.5, 41.0, 61.2, 169.8.

***trans*-*N*-Methoxy-*N*-methyl-3-(2-phenylethyl)-1H-aziridine-2-carboxamide (III).** *trans*-*N*-Methoxy-*N*-methyl-3-(2-phenylethyl)oxirane-2-carboxamide[28] (1.38 g, 5.89 mmol) was treated to the two-step procedure described above. Flash chromatography (1.5:1 EtOAc/CH_2Cl_2) provided an inseparable mixture of the title compound and triphenylphosphine oxide. Repeated purification provided sufficient product for characterization purposes only. Generally the mixture was purified after nitrogen protection: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50-1.60 (bs, 1H), 1.69-1.85 (m, 2H), 2.11 (bs, 1H), 2.68-2.84 (m, 3H), 3.21 (s, 3H), 3.71 (s, 3H), 7.14-7.18 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6, 33.3, 33.4, 38.5, 61.7, 125.8, 128.3, 128.3, 141.2, 171.5.

***trans*-*N*,*N*-Diethyl-3-methyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxamide (7b).** To a 0 °C solution of *N*,*N*-diethyl-3-methyl-1H-aziridine-2-carboxamide (400 mg, 2.56 mmol) and *p*-toluenesulfonic anhydride (940 mg, 2.88 mmol) in CH_2Cl_2 (15 mL) was added triethylamine (389 mg, 3.84 mmol, 0.53 mL). The reaction mixture was warmed to 23 °C and stirred for 12 h. The reaction mixture was washed with water (5 mL) and dried with anhydrous $MgSO_4$. Flash chromatography (1:1 hexanes/EtOAc) provided 735 mg (92%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.64 (d, J = 6.0 Hz, 3H), 2.41 (s, 3H), 3.18-3.24 (m, 1H), 3.26-3.36 (m, 3H), 3.39 (d, J = 4.2 Hz, 1H), 3.48-3.57 (m, 1H), 7.28-7.30 (m, 2H), 7.83-7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 13.4, 14.4, 21.5, 40.5, 41.7, 43.8, 44.0, 127.4, 129.4, 136.9, 144.2, 164.1.

***trans*-*N*-Methoxy-*N*-methyl-3-methyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxamide (7d).** To a 0 °C solution of aziridine **I** (400 mg, 2.77 mmol) and *p*-toluenesulfonic anhydride (1.36 mg, 4.16 mmol) in CH_2Cl_2 (20 mL) was added triethylamine (561 mg, 5.55 mmol, 0.77 mL). The reaction mixture was warmed to 23 °C and stirred for 12 h. The reaction mixture was washed with water (5 mL) and dried with anhydrous $MgSO_4$. Flash chromatography (1:1 hexanes/EtOAc) provided 627.6 mg (76%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (d, J = 6.1 Hz, 3H), 2.41 (s, 3H), 3.13-3.19 (m, 4H), 3.72 (s, 3H), 3.80 (d, J = 4.0 Hz, 1H), 7.28-7.30 (m, 2H), 7.83-7.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 21.5, 32.4, 41.8, 44.1, 62.0, 127.5, 129.5, 136.9, 144.3, 166.2.

***N*-Methoxy-*N*-methyl-3,3-dimethyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxamide (7e).** To a 0 °C solution of aziridine **II** (200 mg, 1.26 mmol) and *p*-toluenesulfonic anhydride (617 mg, 1.89 mmol) in CH_2Cl_2 (10 mL) was added triethylamine (254 mg, 2.52 mmol, 0.35 mL). The reaction mixture was warmed to 23 °C and stirred for 12 h. The reaction mixture was washed with water (5 mL) and dried with anhydrous $MgSO_4$. Flash chromatography (1:1 hexanes/EtOAc) provided 365.5 mg (93%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 3H), 1.84 (s, 3H), 2.39 (s, 3H), 3.14 (s, 3H), 3.69 (s, 3H), 3.81 (s, 1H), 7.27-7.29 (m, 2H), 7.85-7.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.5, 21.9, 32.3, 49.7, 51.8, 61.6, 127.1, 129.4, 137.5, 143.8, 165.9.

Ethyl *trans*-1-Acetyl-3-Phenylaziridine-2-carboxylate (9a). To a 0 °C solution of aziridine **9h** (500 mg, 2.61 mmol) and triethylamine (528 mg, 5.22 mmol, 0.73 mL) in $CHCl_3$ (4.5 mL) was added acetic anhydride (321 mg, 3.14 mmol, 0.30 mL). The resulting mixture was stirred with warming to 23 °C overnight. The reaction mixture was washed with water (2 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated to provide 560 mg (92%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3H), 2.12 (s, 3H), 3.18 (d, J = 2.2 Hz, 1H), 3.82 (d, J = 2.2 Hz, 1H), 4.21-4.29 (m, 2H), 7.27-7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 23.7, 44.1, 44.8, 62.0, 126.2, 128.5, 128.6, 134.8, 167.2, 178.8.

Ethyl *trans*-3-Phenyl-1-(1,1-dimethylethoxycarbonyl)aziridine-2-carboxylate (9b). To a 0 °C solution of aziridine **9h** (500 mg, 2.61 mmol) and triethylamine (528 mg, 5.22 mmol, 0.73 mL) in $CHCl_3$ (4.5 mL) was added di-*tert*-butyl dicarbonate (685 mg, 3.14 mmol). The resulting mixture was stirred with warming to 23 °C for 24 h. The reaction mixture was washed with water (2 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. The crude residue was purified by flash column chromatography (4:1 hexanes/EtOAc) to provide 263.3 mg (35%) of the title compound and 230 mg (46%) of recovered starting material: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, J = 7.1 Hz, 3H), 1.44 (s, 9H), 3.07 (d, J = 2.5 Hz, 1H), 3.79 (d, J= 2.5 Hz, 1H), 4.17-4.33 (m, 2H), 7.26-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 27.8, 44.0, 44.9, 61.8, 82.0, 126.4, 128.2, 128.4, 135.3, 158.2, 167.3.

Methyl *trans*-1-(1,1-Dimethylethoxycarbonyl)-3-(2-phenylethyl)aziridine-2-carboxylate (9c). To a solution of aziridine **9i** (1.0 g, 4.9 mmol) in CH_3CN (3 mL) was added di-*tert*-butyl dicarbonate (1.6 g, 7.3 mmol) and 4-dimethylaminopyridine (1.2 g, 9.7 mmol). The resulting solution was stirred for 12 h at 23 °C. The reaction mixture was partitioned between CH_2Cl_2 and H_2O (2:1). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. Flash column chromatography (6:1 hexanes/EtOAc) provided 796 mg (46%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H), 1.78-1.84 (m, 2H), 2.71-2.86 (m, 4H), 3.72 (s, 3H), 7.16-7.20 (m, 3H), 7.24-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 32.9, 33.0, 40.6, 43.5, 52.4, 81.8, 126.1, 128.4, 128.5, 140.7, 158.8, 168.6.

Methyl *trans*-1-(9-Fluorenylmethoxycarbonyl)-3-(2-phenylethyl)aziridine-2-carboxylate (9d). To a 0 °C solution of aziridine **9i** (100 mg, 0.49 mmol) in THF/H_2O (2 mL, 1:1) containing sodium carbonate (77 mg, 0.73 mmol) was added a solution of 9-fluorenylmethyl chloroformate (132 mg, 0.51 mmol) in THF (1 mL). The reaction mixture was warmed to 23 °C and stirred for 2 h. Water (4 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography (3:1 hexanes/EtOAc) provided 120.3 mg (81%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79-1.90 (m, 2H), 2.69-2.80 (m, 2H), 2.82-2.86 (m, 2H), 3.65 (s, 3H), 4.23 (t, J = 7.0 Hz, 1H), 4.33 (dd, J = 10.5, 7.3 Hz, 1H), 4.51 (dd, J = 10.6, 6.9 Hz, 1H), 7.17-7.21 (m, 3H), 7.26-7.31 (m, 4H), 7.36-7.40 (m, 2H), 7.40-7.60 (m, 2H), 7.72-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8, 32.8, 40.5, 43.6, 46.7, 52.5, 68.3, 119.9, 124.9, 125.0, 126.1, 127.0, 127.6, 127.7, 128.3, 128.4, 140.5, 141.2, 143.3, 143.6, 160.0, 168.4.

Methyl *cis*-*N*-Acetyl-7-azabicyclo[4.1.0]heptane-1-carboxylate (9e). To a 0 °C solution of methyl *cis*-1H-azabicyclo[4.1.0]heptane-1-carboxylate[23] (500 mg, 3.22 mmol) and triethylamine (652 mg, 6.44 mmol, 0.90 mL) in $CHCl_3$ (5.4 mL) was added acetic anhydride (395 mg, 3.87 mmol, 0.36 mL). The resulting mixture was stirred with warming to 23 °C overnight. The reaction mixture was washed with water (3 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. The crude residue was purified by flash column chromatography (2:1 hexanes/EtOAc) to provide 549 mg (86%) of the title compound: ^{1}H NMR

(400 MHz, $CDCl_3$) δ 1.20-1.36 (m, 2H), 1.38-1.47 (m, 2H), 1.85-1.91 (m, 2H), 1.99-2.06 (m, 1H), 2.01 (s, 3H), 2.28-2.35 (m, 1H), 3.04 (dd, J = 4.1, 2.1 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 19.0, 23.0, 23.1, 23.7, 41.5, 43.6, 52.0, 169.7, 178.9.

Methyl *cis*-*N*-(Ethoxycarbonyl)-7-azabicyclo[4.1.0]heptane-1-carboxylate (9f). To a 0 °C solution of methyl *cis*-1H-azabicyclo[4.1.0]heptane-1-carboxylate (500 mg, 3.22 mmol) and triethylamine (652 mg, 6.44 mmol, 0.90 mL) in $CHCl_3$ (5.4 mL) was added acetic anhydride (395 mg, 3.87 mmol, 0.36 mL). The resulting mixture was stirred with warming to 23 °C overnight. The reaction mixture was washed with water (3 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. The crude residue was purified by flash column chromatography (2:1 hexanes/EtOAc) to provide 549 mg (86%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16-1.24 (m, 1H), 1.22 (dt, J = 7.1, 0.5 Hz, 3H), 1.26-1.33 (m, 1H), 1.37-1.46 (m, 2H), 1.81-1.93 (m, 2H), 2.01-2.08 (m, 1H), 2.22-2.30 (m, 1H), 3.06 (dd, J = 4.8, 1.3 Hz, 1H), 3.70 (d, J = 0.5 Hz, 3H), 4.12 (q, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.2, 19.24, 23.3, 23.9, 42.2, 43.8, 52.3, 61.9, 160.5, 170.0.

Methyl 1-(Triphenylmethyl)aziridine-2-carboxylate (9g). Prepared according to the method reported by Kuyl-Yeheskiely et al.[21b] To a -50 °C solution of *N*-trityl serine methyl ester (4.65 g, 12.86 mmol), Et_3N (3.91 g, 38.6 mmol) in dry toluene (280 mL) was added, slowly via cannula, a solution of sulfuryl chloride (2.17 g, 16.08 mmol, 1.29 mL) in toluene (141 mL). The resulting mixture was stirred at -50 °C for 1 h, then at 23 °C for 16 h. The volume was reduced to approximately 200 mL *in vacuo*. EtOAc (150 mL) was added and the resulting mixture was washed with 10% brine solution, dried with anhydrous $MgSO_4$, and concentrated. The crude residue was purified by flash column chromatography (8:1 hexanes/EtOAc) to provide 3.78 g (86%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (dd, J = 6.2, 1.6 Hz, 1H), 1.87 (dd, J = 6.2, 2.7 Hz, 1H), 2.24 (dd, J = 2.7, 1.6 Hz, 1H), 3.74 (s, 3H), 7.19-7.29 (m, 9H), 7.48-7.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.6, 31.6, 52.0, 74.3, 126.9, 127.6, 127.7, 127.8, 127.9, 129.2, 143.5, 171.9.

Procedure for the Preparation of 9j:

***trans*-*N*-Methoxy-*N*-methyl-1-(1,1-dimethylethoxycarbonyl)-3-methylaziridine-2-carboxamide (IV).** To a solution aziridine **I** (500 mg, 3.47 mmol) in CH_3CN (14mL) was added 4-dimethylaminopyridine (847 mg, 6.93 mmol) and di-*tert*-butyl dicarbonate (1.14 g, 5.20 mmol). The reaction mixture was stirred at 23 °C for 12 h, then the solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (15 mL) and the resulting solution was washed with water (5 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography (2:1 hexanes/EtOAc) provided 436.3 mg (51%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, J = 5.6 Hz, 3H), 1.43 (s, 9H), 2.86-2.91 (m, 1H), 3.23 (s, 3H), 3.27 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 27.9, 32.4, 38.8, 39.1, 62.1, 81.3, 159.5, 167.3.

***trans*-2-Acetyl-1-(1,1-dimethylethoxycarbonyl)-3-methylaziridine (9j).** To a 0 °C solution of aziridine **IV** (300 mg, 1.23 mmol) in THF (12 mL) was added dropwise MeMgBr (0.41 mL, 1.23 mmol, 3.0 M in Et_2O). After 1.5 h, TLC analysis (4:1 hexanes/EtOAc) showed complete consumption of the starting material. The reaction mixture was poured into saturated aqueous NH_4Cl (10 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography (4:1 hexanes/EtOAc) to provide 117.4 mg (48%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, J = 5.5 Hz, 3H), 1.44 (s, 9H), 2.21 (s, 3H), 2.70 (dq, J = 5.5, 2.7 Hz, 1H), 2.90 (d, J = 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 27.9, 28.3, 40.5, 47.6, 81.8, 158.9, 203.0.

Procedure for the preparation of 9k:

***trans*-*N*-Methoxy-*N*-methyl-1-(1,1-dimethylethoxycarbonyl)-3-(2-phenylethyl)aziridine-2-carboxamide (V).** To a solution crude aziridine III (5.89 mmol, mixture with $Ph_3P{=}O$) in CH_3CN (23mL) was added 4-dimethylaminopyridine (1.44 g, 11.8 mmol) and di-*tert*-butyl dicarbonate (1.93 g, 8.84 mmol). The reaction mixture was stirred at 23 °C for 12 h, then the solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (25 mL) and the resulting solution was washed with water (10 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography (4:1 hexanes/EtOAc) provided 429.3 mg (22 % over 3 steps) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H), 1.80-1.84 (m, 2H), 2.72-2.88 (m, 2H), 2.91 (dt, J = 6.2, 2.7 Hz, 1H), 3.21 (s, 3H), 3.26 (s, 1H), 3.74 (s, 3H), 7.14-7.18 (m, 3H), 7.20-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 32.4, 33.0, 38.4, 42.7, 62.0, 81.4, 126.0, 128.4, 141.0, 159.4, 167.1.

***trans*-2-Acetyl-1-(1,1-dimethylethoxycarbonyl)-3-(2-phenylethyl)aziridine (9k).** To a 0 °C solution of aziridine V (400 mg, 1.20 mmol) in THF (12 mL) was added dropwise MeMgBr (0.40 mL, 1.20 mmol, 3.0 M in Et_2O). After 0.5 h, TLC analysis (4:1 hexanes/EtOAc) showed complete consumption of the starting material. The reaction mixture was poured into saturated aqueous NH_4Cl (10 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography (4:1 hexanes/EtOAc) to provide 341.4 mg (98%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H), 1.65-1.74 (m, 1H), 1.94-2.02 (m, 1H), 2.11 (s, 3H), 2.65 (dt, J = 6.3, 2.7 Hz, 1H), 2.72 (dt, J = 13.9, 8.1 Hz, 1H), 2.82-2.89 (m, 2H), 7.16-7.21 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.3, 32.9, 44.9, 46.5, 81.7, 126.1, 128.4, 128.5, 140.6, 159.0, 202.2.

***trans*-2-Benzoyl-1-(1,1-dimethylethoxycarbonyl)-3-(2-phenylethyl)aziridine (9l).** To a 0 °C solution of aziridine V (1.25 g, 3.75 mmol) in THF (35 mL) was added dropwise phenyllithium (2.08 mL, 3.75 mmol, 1.8 M in Et_2O). After 1.0 h, TLC analysis (6:1 hexanes/EtOAc) showed complete consumption of the starting material. The reaction mixture was poured into saturated aqueous NH_4Cl (20 mL) and the resulting mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography (6:1 hexanes/EtOAc) to provide 1.15 g (87%) of the title compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 1.81-1.90 (m, 1H), 1.99-2.07 (m, 1H), 2.73-2.81 (m, 1H), 2.84-2.90 (m, 1H), 2.93 (dt, J = 6.2, 2.6 Hz, 1H), 3.62 (d, J = 2.7 Hz, 1H), 7.10-7.22 (m, 5H), 7.43-7.46 (m, 2H), 7.56-7.60 (m, 1H), 7.83-7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 32.9, 33.3, 43.4, 45.5, 81.7, 126.1, 128.3, 128.4, 128.5, 128.7, 133.6, 136.7, 140.8, 159.4, 193.4.

Procedure for the Preparation of 12a:

2-(Hydroxymethyl)-1-(triphenylmethyl)aziridine (VI). To a 0 °C solution of aziridine **9g** (407 mg, 1.18 mmol) in THF (10 mL) was added diisobutylaluminum hydride (371 mg, 2.61 mmol, 0.46 mL). The reaction mixture was warmed to 23 °C for 2 h, then cooled to 0 °C. The reaction mixture was quenched by the addition of a solution of potassium sodium tartrate (30 mL) and stirred until all of the salts dissolved. The mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography provided 332.2 mg (89%) of the title compound: ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, $J = 6.3$ Hz, 1H), 1.54-1.58 (m, 1H), 1.85 (d, $J = 3.3$ Hz, 1H), 2.19 (dd, $J = 7.9$, 3.6 Hz, 1H), 2.68 (ddd, $J = 11.1$, 7.9, 3.2 Hz, 1H), 3.87 (dt, $J = 11.1$, 3.3 Hz, 1H), 7.19-7.29 (m, 9H), 7.42-7.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 33.1, 61.5, 73.6, 126.7, 127.5, 129.2, 144.2.

1-(Triphenylmethyl)aziridine-2-carbaldehyde (VII). To a 23 °C solution of alcohol **VI** (499.7 mg, 1.58 mmol) and pyridine (375 mg, 4.74 mmol, 0.38 mL) in CH_2Cl_2 (16 mL) was added Dess-Martin periodinane (873 mg, 2.06 mmol). The reaction mixture was stirred for 2 h, then diluted with ether (120 mL). A solution of saturated aqueous sodium bicarbonate and sodium thiosulfate (50 mL) was added. The mixture was stirred for 20 min, then the layers were separated. The aqueous phase was washed with ether (2 x 20 mL). The combined organic phases were washed with saturated aqueous sodium bicarbonate (25 mL), water (25 mL) and then dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography (8:1 hexanes/EtOAc) provided 447 mg (90%) of the title compound: ^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (dd, $J = 6.2$, 0.8 Hz, 1H), 1.92-1.96 (m, 1H), 2.32 (dd, $J = 2.4$, 0.7 Hz, 1H), 7.19-7.29 (m, 9H), 7.43-7.46 (m, 6H), 9.33 (d, $J = 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 38.9, 73.7, 127.1, 127.7, 129.1, 143.3, 200.7.

1-(Triphenylmethyl)-2-[(*E*)-2-(methoxycarbonyl)ethenyl]aziridine (12a). To a solution of aldehyde **VII** (447 mg, 1.43 mmol) in THF (7 mL) was added methyl (triphenylphosphoranylidene)acetate (525 mg, 1.57 mmol). The reaction mixture was heated to reflux for 12 h, then cooled to 23 °C and concentrated. Flash chromatography (10:1 hexanes/EtOAc) provided 524.7 mg (99%) of the title compound: ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (d, $J = 6.2$ Hz, 1H), 1.79-1.83 (m, 1H), 1.91 (d, $J = 2.2$ Hz, 1H), 6.03 (d, $J = 15.7$ Hz, 1H), 6.93 (dd, $J = 15.6$, 8.0 Hz, 1H), 7.18-7.28 (m, 10H), 7.43-7.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 33.0, 51.5, 74.4, 121.5, 126.8, 127.5, 129.4, 143.9, 149.6, 166.7.

Procedure for the Preparation of 12b:

Methyl (2*S*, 3*S*)-3-Methyl-1H-aziridine-2-carboxylate (VIII). To a 0 °C solution of methyl (2*S*, 3*S*)-3-methyl-(1-triphenylmethyl)aziridine-2-carboxylate[31] (5.81 g, 16.0 mmol) in CH_2Cl_2 (9 mL) and MeOH (9 mL) was added trifluoroacetic acid (18 mL). The reaction mixture was warmed to 23 °C and stirred for 4 h. The solvent was removed *in vacuo* (bath temperature: 20 °C). The residue was dissolved in water (20 mL) and washed with ether (2 x 10 mL). After the phases were separated, the pH of the aqueous phase was adjusted to pH 10 (paper) by the addition of saturated aqueous sodium carbonate. The resulting mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated *in vacuo* (bath temperature: 20 °C). The residue was purified by Kugelrohr distillation under aspirator pressure to give 1.45 g (78%) of the title compound: bp 53-65 °C at aspirator pressure; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (bs, 1H), 1.27 (d, $J = 5.7$ Hz, 3H), 2.29 (m, 1H), 2.61 (d, $J = 6.2$ Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 33.5, 34.5, 52.0, 171.1.

(2*S*, 3*S*)-3-Methyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxylic acid (IX). To a 0 °C solution of ester **3d** (1.2 g, 4.46 mmol) in a mixture of CH_3CN (6 mL) and H_2O (6 mL) was added 1 M NaOH (4.68 mL). The reaction mixture was warmed to 23 °C and stirred for 12 h. The reaction mixture was concentrated on a rotary evaporator. The pH of the aqueous residue was adjusted to pH 1-2 (paper) by the addition of 1 M citric acid. The resulting mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and concentrated to provide 1.09 g (96%) of the title compound: ^1H NMR (400 MHz,

$CDCl_3$) δ 1.32 (d, J = 5.8 Hz, 3H), 2.44 (s, 3H), 3.11-3.17 (m, 1H), 3.38 (d, J = 7.8 Hz, 1H), 7.33-7.35 (m, 2H), 7.81-7.83 (m, 2H); ^{13}C NMR (100 MHz,) δ 12.1, 21.6, 40.4, 40.8, 127.9, 129.9, 133.8, 145.2, 171.2.

Methyl (2*S*, 2'*S*, 3*S*, 3'*S*)-3-Methyl-1-[3'-methyl-1'-(*p*-toluenesulfonyl)aziridine-2'-carbonyl]aziridine-2-carboxylate (12b). To a 0 °C of carboxylic acid **IX** (444 mg, 1.74 mmol) and NH aziridine **VIII** (200 mg, 1.74 mmol) in $CHCl_3$ (13 mL) was added a solution of dicyclohexylcarbodiimide (359 mg, 1.74 mmol) in $CHCl_3$ (3.5 mL). The resulting mixture was stirred 12 h at 23 °C. The reaction mixture was filtered through Celite. The filtrate was washed with 1 N aqueous sodium bicarbonate (5 mL), 10% aqueous citric acid (5 mL) and water (5 mL). The organic phase was dried with anhydrous $MgSO_4$ and concentrated. Flash chromatography (2:1 hexanes/EtOAc) provided 524.3 mg (86%) of the title compound: ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, J = 5.6 Hz, 3H), 1.34 (d, J = 5.7 Hz, 3H), 2.44 (s, 3H), 2.82 (dq, J = 6.0, 5.7 Hz, 1H), 3.05 (dq, J = 11.7, 7.5, 5.7 Hz, 1H), 3.16 (d, J = 6.2 Hz, 1H), 3.36 (d, J = 7.7 Hz, 1H), 3.75 (s, 3H), 7.33-7.35 (m, 2H), 7.76-7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 12.6, 21.6, 38.0, 39.7, 41.9, 42.6, 52.2, 127.9, 129.8, 134.1, 145.1, 167.0, 176.0.

General Procedure for the Reduction of 2-Acetylaziridines with SmI_2. To a suspension of Sm powder (370 mg, 2.46 mmol) in THF (9.8 mL) at 23 °C was added diiodomethane (549.1 mg, 2.05 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to 0 °C (ice/water) and treated with the aziridine (1 mmol) in MeOH (1 mL) and THF (4 mL). The reaction mixture was stirred for 5 min at 0 °C, quenched at this temperature by the addition of saturated aqueous sodium bicarbonate, then warmed to room temperature. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate.

***N*-(1-Phenyl-3-oxobutyl) *p*-Toluenesulfonamide (4a).** Using the general procedure above, **3a** (216.5 mg, 0.69 mmol) was reduced at 0 °C to provide 177.7 mg (82%) of the title compound after flash chromatography (2:1 hexanes/EtOAc): mp 106-107.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.35 (s, 3H), 2.88 (dd, J = 17.3, 6.2 Hz, 1H), 3.02 (dd, J = 17.3, 5.6 Hz, 1H), 4.66 (m, 1H), 5.62 (d, J = 7.2 Hz, 1H), 7.04-7.07 (m, 2H), 7.14-7.17 (m, 5H), 7.56-7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 30.6, 49.6, 54.1, 126.5, 127.1, 127.6, 128.5, 129.4, 137.2, 139.7, 143.2, 206.5; IR (CH_2Cl_2) 3277, 3062, 3031, 2922, 1709, 1598, 1495, 1456, 1327, 1158 cm^{-1}; HRMS calcd for $C_{17}H_{19}NO_3SH$: 318.1164, found 318.1151; LRMS (EI+) *m/z* 318. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 64.33; H, 6.03; N, 4.41. Found: C, 64.64; H, 6.36; N, 4.27.

***N*-(3-Oxobutyl) *p*-Toluenesulfonamide (4b).** Using the general procedure above, **3b** (164.3 mg, 0.69 mmol) was reduced with SmI_2 (1.41 mmol) at 0 °C to provide 131.2 mg (79%) of the title compound after flash chromatography (1:1 hexanes/EtOAc): mp 69-71.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.40 (s, 3H), 2.67 (t, J = 5.7 Hz, 2H), 3.08-3.13 (m, 2H), 5.06 (t, J = 6.0 Hz, 1H), 7.27-7.29 (m, 2H), 7.70-7.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 30.0, 38.0, 42.9, 127.0, 129.7, 136.9, 143.4, 207.8; IR ($CDCl_3$) 3278, 2924, 1711, 1598, 1494, 1420, 1358, 1327, 1168, 1092 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO_3S$ (M+H): 242.0851, found 242.0852; LRMS (CI-) *m/z* 240. Anal. Calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80. Found: C, 55.06; H, 6.37; N, 5.85.

***N*-(1,1-Dimethyl-3-oxobutyl) *p*-Toluenesulfonamide (4c).** Using the general procedure above, **3c** (141.9 mg, 0.53 mmol) was reduced with SmI_2 (1.09 mmol) at 0 °C to provide 125.3 mg (88%) of the title compound after flash chromatography (2:1 hexanes/EtOAc): mp 67-69 °C; ^1H NMR (400 MHz, $CDCl_3$) δ

1.21 (s, 6H), 2.03 (s, 3H), 2.39 (s, 3H), 2.60 (s, 2H), 5.78 (s, 1H), 7.24-7.26 (m, 2H), 7.71-7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 27.7, 31.3, 53.2, 54.7, 127.0, 129.4, 140.0, 142.9, 208.3; IR ($CDCl_3$) 3295, 2979, 2927, 1706, 1599, 1496, 1385, 1366, 1323, 1202, 1155, 1094, 1021, 992, 816, 665 cm^{-1}; HRMS calcd for $C_{12}H_{16}NO_3S$ (M-CH_3): 254.0851, found 254.0846; LRMS (EI+) *m/z* 254 (M-CH_3). Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20. Found: C, 58.24; H, 7.39; N, 5.22.

***N*-(3-Oxocyclohexyl) *p*-Toluenesulfonamide (4d).** Using the general procedure above, **3d** (198.2 mg, 0.75 mmol) was reduced with SmI_2 (1.53 mmol) at 0 °C to provide 164.7 mg (82%) of the title compound after flash chromatography (1:1 hexanes/EtOAc): mp 117-120 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50-1.66 (m, 2H), 1.90-1.97 (m, 2H), 2.14-2.29 (m, 3H), 2.40 (s, 3H), 2.46 (dd, *J* = 14.3, 4.7 Hz, 1H), 3.44-3.55 (m, 1H), 5.27 (d, *J* = 7.3 Hz, 1H), 7.26-7.29 (m, 2H), 7.71-7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.6, 31.8, 40.5, 48.4, 52.4, 126.9, 129.8, 137.5, 143.7, 208.1; IR ($CDCl_3$) 3267, 2951, 1711, 1598, 1495, 1449, 1327, 1258, 1223, 1159, 1091, 816 cm^{-1}; HRMS calcd for $C_{13}H_{17}NO_3S$: 267.0929, found 267.0931; LRMS (EI+) *m/z* 267. Anal. Calcd for $C_{13}H_{17}NO_3S$: C, 58.41; H, 6.41; N, 5.24. Found: C, 58.73; H, 6.56; N, 4.95.

4-(1,1-Dimethylethoxycarbamido)pentan-2-one (10j). Using the general procedure above, **9j** (50.0 mg, 0.25 mmol) was reduced with SmI_2 (0.51 mmol) at 0 °C to provide 46.2 mg (92%) of the title compound after flash chromatography (4:1 hexanes/EtOAc): ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, *J* = 6.7 Hz, 3H), 1.41 (s, 9H), 2.13 (s, 3H), 2.55 (dd, *J* = 16.4, 6.3 Hz, 1H), 2.67 (dd, *J* = 16.5, 5.2 Hz, 1H), 3.96-4.02 (m, 1H), 4.82 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 28.3, 30.5, 43.2, 49.6, 79.2, 155.1, 207.6; IR (neat) 3346, 2976, 2932, 1712, 1520, 1455, 1391, 1366, 1250, 1172 cm^{-1}; HRMS calcd for $C_{10}H_{20}NO_3$ (M+H): 202.1443, found 202.1451; LRMS (CI + NH_3) *m/z* 202 (M+H).

4-(1,1-Dimethylethoxycarbamido)-6-phenylhexan-2-one (10k). Using the general procedure above, **9k** (50.0 mg, 0.17 mmol) was reduced with SmI_2 (0.35 mmol) at 0 °C to provide 47.9 mg (97%) of the title compound after flash chromatography (2:1 hexanes/EtOAc): mp 94-96.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 1.72-1.91 (m, 2H), 2.10 (s, 3H), 2.54-2.73 (m, 4H), 3.85-3.95 (m, 1H), 4.94 (d, *J* = 7.4 Hz, 1H), 7.14-7.17 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 30.4, 32.7, 36.4, 47.3, 48.1, 79.2, 125.9, 128.3, 128.4, 141.5, 155.4, 207.8; IR (CH_2Cl_2) 3346, 3026, 2976, 1711, 1497, 1365, 1170 cm^{-1}; HRMS calcd for $C_{17}H_{26}NO_3$ (M+H): 292.1912, found 292.1916; LRMS (EI) *m/z* 291. Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.71; H, 8.91; N, 4.97.

General Procedure for the Reduction of Aziridine-2-carboxylate Esters with SmI_2. To a suspension of Sm powder (451 mg, 3.0 mmol) in THF (6.0 mL) at 23 °C was added diiodomethane (669.7 mg, 2.50 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to 0 °C (ice/water) and treated with the aziridine (1 mmol) and *N,N*-dimethylethanolamine (DMEA) (446 mg, 5.0 mmol) in THF (2 mL). The reaction mixture was stirred for 5 min at 0 °C, quenched at this temperature by the addition of saturated aqueous sodium bicarbonate, then warmed to room temperature. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate.

Ethyl 3-Phenyl-3-(*p*-toluenesulfonamido)propanoate (6a). Using the general procedure above, **5a** (224.2 mg, 0.65 mmol) was reduced to provide 196.1 mg (87%) of the title compound after flash chromatography (3:1 hexanes/EtOAc): mp 78-81 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 2.72 (dd, J = 15.9, 6.1 Hz, 1H), 2.81 (dd, J = 15.9, 6.1 Hz, 1H), 3.96-4.01 (m, 2H), 4.70 (q, J = 7.6 Hz, 1H), 5.63 (d, J = 7.7 Hz, 1H), 7.07-7.10 (m, 2H), 7.14-7.18 (m, 5H), 7.57-7.59 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.9, 21.4, 41.3, 54.3, 60.8, 126.4, 127.0, 127.6, 128.4, 129.4, 137.4, 139.3, 143.2, 170.6; IR (CDCl$_3$) 3278, 3064, 3031, 2982, 2928, 1733, 1598, 1331, 1160 cm^{-1}; HRMS calcd for $C_{18}H_{21}NO_4SH^+$: 348.1270, found 348.1266; LRMS (EI+) *m/z* 348 (M+H). Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09; N, 4.03. Found: C, 62.13; H, 6.18; N, 4.01.

Ethyl 3-(*p*-Toluenesulfonamido)propanoate (6b). Using the general procedure above, **5b** (193 mg, 0.72 mmol) was reduced to provide 191.5 mg (98%) of the title compound after flash chromatography (2:1 hexanes/EtOAc): mp 47-49 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.20 (t, J = 7.1 Hz, 3H), 2.39 (s, 3H), 2.49 (t, J = 6.0 Hz, 2H), 3.15 (q, J = 6.2 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 7.27-7.29 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.0, 21.4, 34.0, 38.6, 60.8, 126.9, 129.6, 136.8, 143.3, 171.8; IR (CDCl$_3$) 3286, 2983, 2931, 1732, 1598, 1495, 1422, 1378, 1329, 1290, 1186, 1160, 1094, 1051, 1026, 816, 666 cm^{-1}; HRMS calcd for $C_{12}H_{18}NO_4S$ (M+H): 272.0956, found 272.0933; LRMS (EI+) *m/z* 272 (M+H). Anal. Calcd for $C_{12}H_{17}NO_4S$: C, 53.12; H, 6.31; N, 5.16. Found: C, 52.81; H, 6.50; N, 5.42.

Methyl 3-Methyl-3-(*p*-toluenesulfonamido)butanoate (6c). Using the general procedure above, **5c** (200 mg, 0.74 mmol) was reduced to provide 175.2 mg (87%) of the title compound after flash chromatography (2:1 hexanes/EtOAc): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.25 (s, 3H), 2.39 (s, 3H), 2.46 (s, 2H), 3.65 (s, 3H), 5.69 (s, 1H), 7.24-7.26 (m, 2H), 7.74-7.76 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.4, 27.6, 45.7, 51.6, 54.5, 127.0, 129.4, 140.1, 143.0, 171.8; IR (neat) 3291, 2981, 2952, 1735, 1437, 1389, 1321, 1223, 1155, 1093 cm^{-1}; HRMS calcd for $C_{13}H_{20}NO_4S$ (M+H): 286.1113, found 286.1117; LRMS (EI$^+$) *m/z* 285.

Methyl (3*S*)-3-(*p*-Toluenesulfonamido)butanoate (6d). Using the general procedure above, **5d** (200 mg, 0.74 mmol) was reduced to provide 172.5 mg (86%) of the title compound after flash chromatography (2:1 hexanes/EtOAc): mp 84-85.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.12 (d, J = 6.7 Hz, 3H), 2.40 (s, 3H), 2.41 (d, J = 5.6 Hz, 2H), 3.60 (s, 3H), 3.61-3.70 (m, 1H), 5.12 (d, J = 8.4 Hz, 1H), 7.27-7.29 (m, 2H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.0, 21.5, 40.5, 46.5, 51.7, 127.0, 129.7, 137.9, 143.3, 171.5; IR (CDCl$_3$) 3282, 2954, 1738, 1598, 1494, 1436, 1368, 1333, 1259, 1199, 1161, 1090 cm^{-1}; HRMS calcd for $C_{11}H_{14}NO_4S$ (M-CH$_3$): 256.0644, found 256.0634; LRMS (EI+) *m/z* 256 (M-CH$_3$). $[\alpha]^{20}_D$ -28.4 (c = 1 m, CHCl$_3$). Anal. Calcd for $C_{12}H_{17}NO_4S$: C, 53.12; H, 6.32; N, 5.16. Found: C, 53.36; H, 6.53; N, 5.20.

Ethyl 3-Acetamido-3-phenylpropanoate (10a). Using the general procedure above, **9a** (250 mg, 1.07 mmol) was reduced to provide 225 mg (89%) of the title compound after flash chromatography (1:1 hexanes/EtOAc): mp 39-41.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.14 (t, J = 7.2 Hz, 3H), 2.00 (s, 3H), 2.79 (dd, J = 15.6, 6.0 Hz, 1H), 2.89 (dd, J = 15.6, 5.9 Hz, 1H), 4.04 (q, J = 7.1 Hz, 2H), 5.41 (dt, J = 8.5, 5.9 Hz, 1H), 6.59 (d, J = 7.5 Hz, 1H), 7.22-7.32 (m, 5H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.9, 23.2, 40.0, 49.5, 60.6, 126.2, 127.5, 128.5, 140.5, 169.2, 171.1; IR (CDCl$_3$) 3280, 3063, 2982, 2935, 1737, 1651, 1547, 1496, 1454, 1373, 1299, 1172, 1097, 1030, 700 cm^{-1}; HRMS calcd for $C_{13}H_{17}NO_3$: 235.1208, found 235.1209; LRMS (EI+) *m/z* 235. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.19; H, 7.49; N, 6.07.

Ethyl 3-(1,1-Dimethylethoxycarbamido)-3-phenylpropanoate (10b). Using the general procedure above, **9b** (255 mg, 0.88 mmol) was reduced to provide 210.6 mg (82%) of the title compound after flash chromatography (3:1 hexanes/EtOAc): mp 61-64 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.14 (t, J = 7.1 Hz, 3H), 1.40 (s, 9H), 2.76-2.82 (m, 2H), 4.04 (q, J = 7.1 Hz, 2H), 5.08 (bs, 1H), 5.43 (bs, 1H), 7.21-7.33 (m, 5H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 14.0, 28.3, 50.0, 51.2, 60.5, 79.5, 126.1, 127.4, 128.5, 141.2, 154.9, 170.8; IR ($CDCl_3$) 3362, 3032, 2979, 2933, 1715, 1604, 1496, 1455, 1392, 1367, 1289, 1247, 1169 cm^{-1}; HRMS calcd for $C_{16}H_{24}NO_4$: 294.1705, found 294.1713; LRMS (EI+) *m/z* 294. Anal. Calcd for $C_{16}H_{24}NO_4$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.50; H, 8.09; N, 4.88.

Methyl 5-Phenyl-3-(1,1-dimethylethoxycarbamoyl)pentanoate (10c). Using the general procedure above, **9c** (150 mg, 0.49 mmol) was reduced to provide 148.1 mg (98%) of the title compound after flash chromatography (4:1 hexanes/EtOAc): mp 64-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 1.74-1.85 (m, 2H), 2.48-2.73 (m, 4H), 3.65 (s, 3H), 3.91-4.00 (m, 1H), 4.98 (d, *J* = 8.6 Hz, 1H), 7.14-7.18 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 32.5, 36.4, 39.1, 47.5, 51.6, 79.3, 125.9, 128.3, 128.4, 141.4, 155.3, 172.0; IR ($CDCl_3$) 3362, 3026, 2977, 2951, 2862, 1738, 1714, 1497, 1454, 1438, 1391, 1366, 1246, 1169, 1049 cm^{-1}; HRMS calcd for $C_{17}H_{26}NO_4$ (M+H): 308.1862, found 308.1855; LRMS ($CI+NH_3$) *m/z* 308 (M+H). Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.70; H, 8.50; N, 4.63.

Methyl 3-(9-Fluorenylmethylcarbamido)-5-phenylpentanoate (10d). Using the general procedure above, **9d** (170.3 mg, 0.40 mmol) was reduced to provide 155.4 mg (91%) of the title compound after flash chromatography (3:1 hexanes/EtOAc): mp 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78-1.96 (m, 2H), 2.51-2.71 (m, 4H), 3.66 (s, 3H), 3.97-4.05 (m, 1H), 4.21 (t, *J* = 6.9 Hz, 1H), 4.36-4.44 (m, 2H), 5.26 (d, *J* = 9.2 Hz, 1H), 7.15-7.19 (m, 3H), 7.24-7.31 (m, 4H), 7.36-7.40 (m, 2H), 7.57-7.59 (m, 2H), 7.74-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.4, 36.0, 38.8, 47.2, 47.8, 51.7, 66.5, 119.9, 125.0, 126.0, 127.0, 127.6, 128.3, 128.4, 141.2, 141.3, 143.8, 143.9, 155.8, 171.9; IR ($CDCl_3$) 3333, 3024, 2948, 1724, 1603, 1523, 1478, 1450, 1242, 1155, 1049 cm^{-1}; HRMS calcd for $C_{27}H_{27}NO_4$: 430.2018, found 430.2053; LRMS ($CI+NH_3$) *m/z* 430. Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.32; H, 6.47; N, 2.92.

Methyl (1*R, 2*S**)-2-(Acetamido)cyclohexanecarboxylate (10e) and Methyl (1*R**, 2*R**)-2-(Acetamido)cyclohexane-1-carboxylate (10e').** Using the general procedure above, **9e** (266 mg, 1.35 mmol) was reduced to provide 125.8 mg (47%) of **10e** and 68.4 mg (25%) of **10e'** after flash chromatography (2:1 hexanes/EtOAc): **10e**: mp 73-75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15-1.25 (m, 1H), 1.34-1.50 (m, 2H), 1.55-1.77 (m, 4H), 1.93 (s, 3H), 2.02-2.09 (m, 1H), 2.79 (dt, *J* = 9.0, 4.5 Hz, 1H), 3.68 (s, 3H), 4.07-4.14 (m, 1H), 6.35 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 23.5, 24.1, 27.2, 29.2, 44.2, 47.7, 51.6, 169.1, 174.6; IR ($CDCl_3$) 3307, 3065, 2936, 2858, 1735, 1651, 1538, 1435, 1375, 1314, 1253, 1214, 1192, 1173, 1132 cm^{-1}; HRMS calcd for $C_{10}H_{17}NO_3$: 199.1208, found 199.1194; LRMS (EI+) *m/z* 199. **10e'**: mp 104-105.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09-1.23 (m, 2H), 1.33-1.40 (m, 1H), 1.55-1.65 (m, 1H), 1.70-1.73 (m, 2H), 1.88-1.95 (m, 1H), 1.90 (s, 3H), 2.02-2.06 (m, 1H), 2.22 (dt, *J* = 11.0, 3.6 Hz, 1H), 3.64 (s, 3H), 3.91-4.00 (m, 1H), 5.34 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 24.4, 24.5, 28.4, 32.7, 49.8, 49.9, 51.8, 169.2, 174.2; IR ($CDCl_3$) 3277, 3078, 2935, 2857, 1738, 1652, 1556, 1434, 1372, 1321, 1281, 1251, 1232, 1191, 1171, 1127, 1028, 722 cm^{-1}; HRMS calcd for $C_{10}H_{17}NO_3$: 199.1208, found 199.1188; LRMS (EI+) *m/z* 199. Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.62; H, 8.86; N, 6.74.

Methyl (1*R, 2*S**)-2-(Ethoxycarbamoyl)cyclohexanecarboxylate (10f) and Methyl (1*R**, 2*R**)-2-(Ethoxycarbamoyl)cyclohexanecarboxylate (10f').** Using the general procedure above, **9f** (249.6 mg, 1.10 mmol) was reduced to provide 51.3 mg (20%) of **10f** and 127.8 mg (51%) of **10f'** after flash chromatography

(4:1 hexanes/EtOAc): **10f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.1 Hz, 3H), 1.25-1.42 (m, 3H), 1.56-1.66 (m, 3H), 1.71-1.77 (m, 1H), 1.94-2.02 (m, 1H), 2.77 (q, *J* = 4.7 Hz, 1H), 3.66 (s, 3H), 3.82-3.87 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 5.43 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 22.5, 23.7, 26.8, 29.6, 44.7, 49.4, 51.5, 60.6, 155.9, 174.3; IR ($CDCl_3$) 3437, 3345, 2935, 2859, 1720, 1509, 1451, 1436, 1312, 1237, 1195, 1174, 1138, 1128, 1104, 1052, 995 cm^{-1}; HRMS calcd for $C_{11}H_{19}NO_4$: 229.1314, found 229.1324; LRMS (EI+) *m/z* 229. **10f'**: mp 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11-1.23 (m, 5H), 1.30-1.43 (m, 1H), 1.52-1.63 (m, 1H), 1.68-1.76 (m, 2H), 1.87-1.93 (m, 1H), 2.02-2.10 (m, 1H), 2.23 (t, *J* = 8.0 Hz, 1H), 3.65 (s, 3H), 3.65-3.76 (m, 1H), 4.06 (q, *J* = 6.7 Hz, 2H), 4.56 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 24.2, 24.5, 28.5, 32.7, 49.6, 51.4, 51.6, 60.4, 155.6, 174.3; IR ($CDCl_3$) 3333, 2980, 2935, 2859, 1732, 1715, 1694, 1538, 1450, 1435, 1372, 1318, 1264, 1232, 1206, 1172, 1125, 1054 cm^{-1}; HRMS calcd for $C_{11}H_{19}NO_4$: 229.1314, found 229.1313; LRMS (EI+) *m/z* 229. Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.62; H, 8.35; N, 6.11. Found: C, 57.61; H, 8.69; N, 6.11.

Methyl 3-(*N*-Triphenylmethylamino)propanoate (10g). Using the general procedure above, **9g** (250 mg, 0.73 mmol) was reduced to provide 206 mg (82%) of the title compound after flash chromatography (6:1 hexanes/EtOAc): mp 85-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (bs, 1H), 2.38 (t, *J* = 6.3 Hz, 2H), 2.50 (t, *J* = 6.3 Hz, 2H), 3.67 (s, 3H), 7.14-7.19 (m, 3H), 7.23-7.28 (m, 6H), 7.44-7.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.2, 39.3, 51.5, 70.8, 126.2, 127.8, 128.5, 145.9, 173.2; IR (CH_2Cl_2) 3324, 3056, 3020, 2949, 1735, 1595, 1489, 1447, 1207, 1169 cm^{-1}; HRMS calcd for $C_{23}H_{23}NO_2$: 345.1729, found 345.1724; LRMS (EI+) *m/z* 345. Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 79.83; H, 6.85; N, 4.07.

Ethyl 3-Amino-3-phenylpropanoate (10h). Using the general procedure above, **9h** (200 mg, 1.05 mmol) was reduced to provide 56.2 mg (28%) of the title compound and 33 mg (16%) of *N*-benzyl glycine ethyl ester after flash chromatography (3:1 EtOAc/hexanes): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.76 (bs, 2H), 2.62 (d, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 4.39 (t, *J* = 6.9 Hz, 1H), 7.20-7.24 (m, 1H), 7.28-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 44.1, 52.6, 60.4, 126.1, 127.3, 128.5, 144.6, 171.9; IR (neat) 3292, 3030, 2980, 1732, 1654, 1542, 1177, 1095 cm^{-1}; HRMS calcd for $C_{11}H_{15}NO_2$: 193.1103, found 193.1104; LRMS (EI) *m/z* 193.

Methyl 3-Amino-5-phenylpentanoate (10i). Using the general procedure above, **9i** (150 mg, 0.73 mmol) was reduced to provide 100.2 mg (66%) of the title compound after flash chromatography using pH 7 silica gel (EtOAc): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (q, *J* = 7.5 Hz, 2H), 2.41 (dd, *J* = 16.1, 8.7 Hz, 1H), 2.56 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.61-2.77 (m, 2H), 3.16 (bs, 2H), 3.25-3.32 (m, 1H), 3.67 (s, 3H), 7.14-7.20 (m, 3H), 7.24-7.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.3, 38.3, 41.1, 48.1, 51.8, 126.0, 128.3, 128.4, 141.2, 172.7; IR (neat) 3243, 3060, 3026, 3000, 2949, 2857, 1732, 1654, 1602, 1496, 1454, 1437, 1203, 1160 cm^{-1}; HRMS calcd for $C_{12}H_{17}NO_2$: 207.1259, found 207.1262; LRMS (EI) *m/z* 207.

3-(1,1-Dimethylethoxycarbamido)-5-phenylpentanophenone (10l). To a suspension of Sm powder (51 mg, 0.34 mmol) in THF (1.0 mL) at 23 °C was added diiodomethane (76 mg, 0.28 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to -78 °C and treated with **9l** (40.0 mg, 0.11 mmol) in MeOH (0.1 mL) and THF (0.5 mL). The reaction mixture was stirred for 5 min at 0 °C, quenched at this temperature by the addition of saturated aqueous sodium bicarbonate, then warmed to room temperature. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate. The crude material was purified by flash chromatography (5:1 hexanes/EtOAc) to provide 33.1 mg (82%) of the title compound: mp 110.5-113.5 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.41 (s, 9H), 1.82-1.91 (m, 1H), 1.94-2.04 (m, 1H), 2.59-2.66 (m, 1H), 2.69-2.77 (m, 1H), 3.12 (dd, J = 16.5, 5.4 Hz, 1H), 3.27-3.33 (m, 1H), 4.05-4.09 (m, 1H), 5.14 (d, J = 7.5 Hz, 1H), 7.12-7.16 (m, 3H), 7.22-7.26 (m, 2H), 7.41-7.45 (m, 2H), 7.52-7.56 (m, 1H), 7.89-7.91 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 28.4, 32.8, 36.1, 42.7, 47.8, 79.2, 125.9, 128.0, 128.3, 128.4, 128.6, 133.3, 136.9, 141.5, 155.5, 199.1; IR (KBr) 3356, 3085, 3061, 3026, 2976, 2929, 2860, 1693, 1598, 1514, 1496, 1450, 1391, 1366, 1247, 1170 cm^{-1}; HRMS calcd for $C_{22}H_{28}NO_3$ (M+H): 354.2069, found 354.2102; LRMS (CI$^-$) *m/z* 353. Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.82; H, 8.04; N, 3.92.

General Procedure for the Reduction of Aziridine-2-carboxamides with SmI$_2$. To a suspension of Sm powder (397 mg, 2.64 mmol) in THF (11 mL) at 23 °C was added diiodomethane (589 mg, 2.20 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI$_2$ was cooled to -25 °C and treated with the aziridine (1 mmol) and DMEA (446 mg, 5.0 mmol) in THF (4 mL). The reaction mixture was stirred for 5 min at -25 °C, quenched at this temperature by the addition of 20% aqueous potassium sodium tartrate (Rochelle's salt), then warmed to room temperature. The aqueous phase was extracted with EtOAc (3x20 mL), and the combined extracts were dried with anhydrous magnesium sulfate.

***N*, *N*-Dimethyl-3-(*p*-toluenesulfonamido)propanamide (8a).** Using the general procedure above, **7a** (111.1 mg, 0.41 mmol) was reduced with SmI$_2$ (1.04 mmol) to provide 96.5 mg (86%) of the title compound after flash chromatography using pH 7 silica gel (1:1 hexanes/EtOAc): mp 117.5-120 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.39 (s, 3H), 2.50 (t, J = 5.5 Hz, 2H), 2.89 (s, 3H), 2.90 (s, 3H), 3.13-3.17 (m, 2H), 5.59 (bt, J = 6.5 Hz, 1H), 7.24-7.29 (m, 2H), 7.71-7.73 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.4, 32.9, 35.2, 36.9, 39.2, 126.9, 129.6, 137.2, 143.1, 171.0; IR (CH$_2$Cl$_2$) 3177, 2926, 1641, 1494, 1444, 1420, 1328, 1161, 1095, 1063 cm^{-1}; HRMS calcd for $C_{12}H_{19}N_2O_3S$ (M+H): 271.1116, found 271.1116; LRMS (EI+) *m/z* 271 (M+H). Anal. Calcd for $C_{12}H_{18}N_2O_3S$: C, 53.31; H, 6.71; N, 10.36. Found: C, 53.19; H, 6.94; N, 10.20.

***N*,*N*-Diethyl-3-(*p*-Toluenesulfonamido)butanamide (8b).** Using the general procedure above, **7b** (120.0 mg, 0.39 mmol) was reduced with SmI$_2$ (0.85 mmol) to provide 85.4 mg (70%) of the title compound after flash chromatography using pH 7 silica gel (2:1 hexanes/EtOAc): mp 75.5-77 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.06 (t, J = 7.1 Hz, 6H), 1.15 (d, J = 6.7 Hz, 3H), 2.33 (dd, J = 16.0, 5.1 Hz, 1H), 2.38 (s, 3H), 2.40 (dd, J = 16.0, 4.9 Hz, 1H), 3.16 (q, J = 7.1 Hz, 2H), 3.29 (dq, J = 7.1, 2.4 Hz, 2H), 3.57-3.70 (m, 1H), 6.10-6.20 (s, 1H), 7.24-7.36 (m, 2H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.0, 14.1, 20.9, 21.5, 37.9, 40.1, 42.0, 47.2, 127.0, 129.6, 138.3, 143.0, 169.8; IR (CH$_2$Cl$_2$) 3203, 2975, 2934, 1621, 1455, 1381, 1331, 1162, 1094 cm^{-1}; HRMS calcd for $C_{15}H_{24}N_2O_3S$: 312.1508, found 312.1494; LRMS (EI+) *m/z* 312 (M+H). Anal. Calcd for $C_{15}H_{24}N_2O_3S$: C, 57.67; H, 7.74; N, 8.97. Found: C, 57.95; H, 8.03; N, 8.83.

General Procedure for the Reduction of *N*-methoxy-*N*-methyl Aziridine-2-carboxamides with SmI$_2$. To a suspension of Sm powder (370 mg, 2.46 mmol) in THF (5.0 mL) at 23 °C was added diiodomethane (549 mg, 2.05 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI$_2$ was cooled to -40 °C and treated with the aziridine (1 mmol) and DMEA (446 mg, 5.0 mmol) in THF (2.5 mL). The reaction mixture was stirred for 5 min at -40 °C, quenched at this temperature by the addition of 20% aqueous potassium sodium tartrate (Rochelle's salt), then warmed to room temperature. The aqueous phase was extracted with EtOAc (3x20 mL), and the combined extracts were dried with anhydrous magnesium sulfate.

***N*-Methoxy-*N*-methyl-3-(*p*-toluenesulfonamido)propanamide (8c).** Using the general procedure above, **7c** (101.3 mg, 0.36 mmol) was reduced to provide 71.9 mg (70%) of the title compound after flash chromatography using pH 7 silica gel (1:1 hexanes/EtOAc): mp 94-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.62 (t, *J* = 5.6 Hz, 2H), 3.10 (s, 3H), 3.14 (q, *J* = 11.8, 6.3 Hz, 2H), 3.60 (s, 3H), 5.50 (t, *J* = 6.4 Hz, 1H), 7.25-7.28 (m, 2H), 7.69-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 31.7, 31.8, 38.7, 61.1, 126.9, 129.6, 137.0, 143.2, 172.4; IR ($CDCl_3$) 3276, 2938, 1651, 1598, 1443, 1327, 1160, 1094 cm^{-1}; HRMS calcd for $C_{12}H_{18}N_2O_4S$: 286.0987, found 286.0980; LRMS (EI+) *m/z* 286. Anal. Calcd for $C_{12}H_{18}N_2O_4S$: C, 50.33; H, 6.34; N, 9.78. Found: C, 50.28; H, 6.56; N, 9.64.

***N*-Methyl-3-(*p*-toluenesulfonamido)propanamide (X).** 16mg (19%) of the title compound was obtained as a side-product from the reduction of *N*-Methoxy-*N*-methyl-1-(*p*-toluenesulfonamido)aziridine-2-carboxamide (92.9 mg, 0.33 mmol) with SmI_2 (0.82 mmol) at 0 °C: mp 127-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36-2.39 (m, 5H), 2.74 (d, *J* = 4.8 Hz, 3H), 3.15 (q, *J* = 6.0 Hz, 2H), 5.56 (t, *J* = 5.7 Hz, 1H), 5.65-5.72 (m, 1H), 7.27-7.29 (m, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.2, 35.2, 39.4, 127.0, 129.7, 136.7, 143.4, 171.6; IR (neat) 3385, 3287, 2924, 1651, 1556, 1324, 1157, 1092 cm^{-1}; HRMS calcd for $C_{11}H_{17}N_2O_3S$ (M+H): 257.0960, found 257.0938; LRMS (CI+, NH_3) *m/z* 274.

***N*-Methoxy-*N*-methyl-3-(*p*-toluenesulfonamido)butanamide (8d).** Using the general procedure above, **7d** (101.3 mg, 0.36 mmol) was reduced to provide 71.9 mg (70%) of the title compound after flash chromatography using pH 7 silica gel (1:1 hexanes/EtOAc): mp 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, *J* = 6.7 Hz, 3H), 2.39 (s, 3H), 2.45 (dd, *J* = 16.5, 5.1 Hz, 1H), 2.59 (dd, *J* = 16.0, 4.7 Hz, 1H), 3.08 (s, 3H), 3.58 (s, 3H), 3.66 (m, 1H), 5.66 (s, 1H), 7.26-7.28 (m, 2H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 31.7, 37.4, 46.8, 61.1, 127.0, 129.5, 138.0, 143.0, 171.7; IR ($CDCl_3$) 3266, 2936, 1644, 1330, 1161, 1093 cm^{-1}; HRMS calcd for $C_{13}H_{21}N_2O_4S$ (M+H): 301.1222, found 301.1214; LRMS (CI+NH_3) *m/z* 301. Anal. Calcd for $C_{13}H_{20}N_2O_4S$: C, 51.98; H, 6.71; N, 9.33. Found: C, 52.22; H, 6.85; N, 9.11.

***N*-Methyl 3-(*p*-Toluenesulfonamido)butanamide (8e).** Using the general procedure above, **7d** (57.9 mg, 0.19 mmol) was reduced with SmI_2 (0.97 mmol) in the presence of DMEA (173 mg, 1.94 mmol) to provide 37.6 mg (73%) of the title compound after flash chromatography using pH 7 silica gel (1.5:1 EtOAc/hexanes): mp 123-126.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.7 Hz, 3H), 2.18 (dd, *J* = 14.9, 5.4 Hz, 1H), 2.29 (dd, *J* = 14.9, 5.0 Hz, 1H), 2.40 (s, 3H), 2.74 (d, *J* = 4.8 Hz, 3H), 3.57-3.63 (m, 1H), 5.58 (bs, 1H), 5.74 (bs, 1H), 7.27-7.29 (m, 2H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.5, 26.1, 41.9, 47.3, 127.0, 129.7, 137.8, 143.3, 171.1; IR ($CDCl_3$) 3386, 3288, 2973, 2930, 1650, 1556, 1412, 1322, 1304, 1159 cm^{-1}; HRMS calcd for $C_{12}H_{19}N_2O_3S$ (M+H): 271.1116, found 271.1126; LRMS (CI + NH_3) *m/z* 271 (M+H).

***N*-Methyl-3,3-dimethyl-1-(*p*-toluenesulfonyl)aziridine-2-carboxamide (7f).** Using the general procedure above, **7e** (120 mg, 0.38 mmol) was reduced to provide 65.1 mg (60%) of the title compound after flash chromatography (1.5:1 EtOAc/hexanes): mp 123-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 3H), 1.72 (s, 3H), 2.44 (s, 3H), 2.65 (d, *J* = 5.0 Hz, 3H), 3.48 (s, 1H), 5.82 (s, 1H), 7.32-7.35 (m, 2H), 7.80-7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 21.5, 21.6, 25.7, 51.0, 53.3, 127.3, 129.9, 136.9, 144.7, 166.0; IR

($CDCl_3$) 3318, 1664 cm^{-1}; HRMS calcd for $C_{13}H_{19}N_2O_3S$ (M+H): 283.1116, found 283.1125; LRMS (EI) *m/z* 282. Anal. Calcd for $C_{13}H_{18}N_2O_3S$: C, 55.30; H, 6.43; N, 9.92. Found: C, 55.44; H, 6.71; N, 9.76.

(2*R, 3*R**) and (2*R**,3*S**)-2-(1-Phenylmethyl)-3-(1,1-dimethylethoxy-carbamoyl)-5-phenylpentanophenone (11a).** To a suspension of Sm powder (85 mg, 0.56 mmol) in THF (5.6 mL) at 23 °C was added diiodomethane (137.2 mg, 0.51 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to -78 °C and treated with hexamethylphosphoramide (HMPA) (459 mg, 2.56 mmol). After 10 min, **9l** (60 mg, 0.17 mmol) in THF (1.0 mL) was added to the purple solution. The reaction mixture was stirred for 5 min at -78 °C, then benzyl bromide (117 mg, 0.68 mmol) was added. The reaction mixture was stirred overnight with warming to 23 °C, and quenched by the addition of saturated aqueous sodium bicarbonate. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate. The crude residue was purified by flash chromatography (silica gel) (8:1 hexanes/EtOAc) to provide 33.8 mg (62%) of the title compound as a 4.7:1 mixture of diastereomers: Major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 9H), 1.55-1.73 (m, 2H), 2.46-2.54 (m, 1H), 2.59-2.67 (m, 1H), 2.91 (dd, *J* = 13.5, 6.6 Hz, 1H), 3.03 (dd, *J* = 13.6, 7.3 Hz, 1H), 3.89-3.94 (m, 1H), 3.95-4.02 (m, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 6.99-7.01 (m, 2H), 7.08-7.22 (m, 8H), 7.35-7.42 (m, 2H), 7.48-7.52 (m, 1H), 7.75-7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 32.9, 36.1, 36.4, 50.0, 51.9, 79.1, 125.8, 126.4, 128.2, 128.3, 128.5, 128.7, 129.0, 133.3, 137.4, 139.1, 141.6, 156.0, 204.6; IR ($CDCl_3$) 3424, 3026, 2976, 1709, 1676, 1596, 1496, 1448, 1366, 1233, 1169 cm^{-1}; HRMS calcd for $C_{29}H_{34}NO_3$ (M+H): 444.2539, found 444.2393; LRMS (EI$^+$) *m/z* 444 (M+H).

(2*R, 3*R**) and (2*R**,3*S**)-3-(1,1-Dimethylethoxycarbamoyl)-2-(2-propenyl)-5-phenylpentanophenone (11b).** To a suspension of Sm powder (85 mg, 0.56 mmol) in THF (5.6 mL) at 23 °C was added diiodomethane (137.2 mg, 0.51 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to -78 °C and treated with hexamethylphosphoramide (HMPA) (459 mg, 2.56 mmol). After 10 min, **9l** (60 mg, 0.17 mmol) in THF (1.0 mL) was added to the purple solution. The reaction mixture was stirred for 5 min at -78 °C, then allyl bromide (92.2 mg, 0.68 mmol) was added. The reaction mixture was stirred overnight with warming to 23 °C, and quenched by the addition of saturated aqueous sodium bicarbonate. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate. The crude residue was purified by flash chromatography (silica gel) (8:1 hexanes/EtOAc) to provide 33.8 mg (51%) of the title compound as a 5.2:1 mixture of diastereomers: Major diastereomer: ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H), 1.57-1.75 (m, 2H), 2.34-2.49 (m, 2H), 2.51-2.59 (m, 1H), 2.63-2.70 (m, 1H), 3.70-3.74 (m, 1H), 3.97-4.04 (m, 1H), 4.99 (d, *J* = 10 Hz, 1H), 5.05 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.69 (d, *J* = 9.7 Hz, 1H), 5.71-5.82 (m, 1H), 7.04-7.12 (m, 3H), 7.17-7.21 (m, 2H), 7.43-7.47 (m, 2H), 7.55-7.58 (m, 1H), 7.90-7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 33.0, 34.5, 36.4, 48.7, 51.5, 79.0, 117.5, 125.8, 128.3, 128.8, 133.5, 135.0, 137.2, 141.7, 156.0, 204.3; IR ($CDCl_3$) 3427, 3026, 2977, 2929, 1710, 1676, 1496, 1235, 1170 cm^{-1}; HRMS calcd for $C_{25}H_{32}NO_3$ (M+H): 394.2382, found 394.2403; LRMS (CI + NH_3) *m/z* 394 (M+H).

Methyl (*E*)- and (*Z*)-5-(*N*-Triphenylmethylamino)-3-pentenoate (13a). Using the general procedure for the reduction of aziridine-2-carboxylate esters, alkenylaziridine **12a** (250 mg, 0.68 mmol) was reduced to give 223.1 mg (88%) of the title compound as a 2:1 mixture of olefinic isomers after flash chromatography (6:1 hexanes/EtOAc): ^1H NMR (400 MHz, $CDCl_3$) δ 1.63 (bs, 2H), 2.71 (s, 2H), 2.75 (d, *J* = 6.7 Hz, 1H), 2.83 (d, $J = 6.8$ Hz, 1H), 3.05-3.06 (m, 1H), 3.60 (s, 1.5H), 3.67 (s, 3H), 5.55-5.61 (m, 0.6H), 5.70-5.72 (m, 2H), 5.74-5.80 (m, 0.6H), 7.14-7.19 (m, 5H), 7.23-7.28 (m, 11H), 7.44-7.47 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6, 37.7, 40.7, 45.5, 51.7, 70.7, 70.9, 122.4, 122.5, 126.2, 126.2, 127.8, 128.3, 131.7, 133.1, 145.8, 145.9, 171.9, 172.2; IR ($CDCl_3$) 3323, 3083, 3057, 3029, 2950, 2843, 1739, 1596, 1490, 1448, 1436, 1335, 1253, 1205, 1163, 1103, 1032 cm^{-1}; HRMS calcd for $C_{25}H_{25}NO_2$: 371.1885, found 371.1892; LRMS (EI) *m/z* 371.

Methyl (3*S*, 3'*S*)-3-[3'-(*p*-Toluenesulfonamido)butanamoyl]butanoate (13b). To a suspension of Sm powder (205 mg, 1.36 mmol) in THF (3.0 mL) at 23 °C was added diiodomethane (304 mg, 1.14 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to 0 °C and treated with bis-aziridine **12b** (80 mg, 0.23 mmol) and DMEA (202 mg, 2.27 mmol) in THF (1.0 mL). The reaction mixture was stirred for 5 min at 0 °C, quenched at this temperature by the addition of saturated aqueous sodium bicarbonate, then warmed to 23 °C. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate. The crude residue was purified by flash chromatography (silica gel) (1:1 hexanes/EtOAc) to provide 67.6 mg (82%) of the title compound: mp 107-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, $J = 6.7$ Hz, 3H), 1.16 (d, $J = 6.8$ Hz, 3H), 2.14 (dd, $J = 14.8, 5.6$ Hz, 1H), 2.24 (dd, $J = 14.7, 5.0$ Hz, 1H), 2.39 (s, 3H), 2.46 (dd, $J = 15.8, 5.1$ Hz, 1H), 2.51 (dd, $J = 15.2, 4.7$ Hz, 1H), 3.55-3.63 (m, 1H), 3.66 (s, 3H), 4.24-4.30 (m, 1H), 5.78 (bs, 1H), 5.13 (d, $J = 8.1$ Hz, 1H), 7.26-7.28 (m, 2H), 7.73-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.9, 21.4, 39.8, 42.0, 47.3, 51.7, 127.0, 129.6, 137.9, 143.2, 169.7, 172.0; IR ($CDCl_3$) 3356, 3280, 2975, 2933, 1734, 1648, 1598, 1545, 1496, 1438, 1159, 1093 cm^{-1}; HRMS calcd for $C_{16}H_{25}N_2O_5S$ (M+H): 357.1484, found 357.1472; LRMS (EI) *m/z* 357. $[\alpha]^{20}_D$ -40.5 (c = 1 m, $CHCl_3$).

Methyl 3-(*N*-(1-Phenylmethyl)carbamido)propanoate (13c). To a suspension of Sm powder (180.6 mg, 1.20 mmol) in THF (5.0 mL) at 23 °C was added diiodomethane (306.8 mg, 1.15 mmol). The resultant olive-green slurry was stirred at ambient temperature for 2 h, after which time the resulting dark blue slurry of SmI_2 was cooled to 0 °C and treated with azetidinone **12c** (81 mg, 0.37 mmol) and DMEA (204 mg, 2.29 mmol) in THF (1.2 mL). The reaction mixture was stirred for 5 min at 0 °C, quenched at this temperature by the addition of saturated aqueous sodium bicarbonate, then warmed to 23 °C. The aqueous phase was extracted with CH_2Cl_2 (5x10 mL), and the combined extracts were dried with anhydrous magnesium sulfate. The crude residue was purified by flash chromatography (silica gel) (1:1 hexanes/EtOAc) to provide 59.1 mg (72%) of the title compound: mp 61-64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (t, $J = 6.7$ Hz, 2H), 2.69 (t, $J = 6.7$ Hz, 2H), 3.66 (s, 3H), 4.34 (d, $J = 5.7$ Hz, 2H), 5.94 (s, 1H), 7.23-7.27 (m, 3H), 7.29-7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.2, 30.8, 43.5, 51.2, 127.4, 127.6, 128.6, 138.2, 171.2, 173.4; IR ($CDCl_3$) 3304, 3030, 2951, 1738, 1651, 1546, 1496, 1454, 1437, 1168 cm^{-1}; HRMS calcd for $C_{12}H_{15}NO_3$: 221.1052, found 221.1052; LRMS (EI) *m/z* 221. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.13; H, 7.06; N, 6.04.

***N*-Benzylacetamide (XI).** 15 mg (27%) of the title compound was obtained as a side product from the reduction of 1-benzyl-4-(methoxycarbonyl)-2-azetidinone (81 mg, 0.37 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 4.64 (s, 2H), 7.26-7.31 (m, 3H), 7.36-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1, 42.3, 127.9, 128.6, 128.8, 135.7, 176.8; IR (neat) 3444, 1694 cm^{-1}.

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