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[5 + 2] Cycloaddition Reaction of 2-Vinylaziridines and Sulfonyl Isocyanates. Synthesis of Seven-Membered Cyclic Ureas

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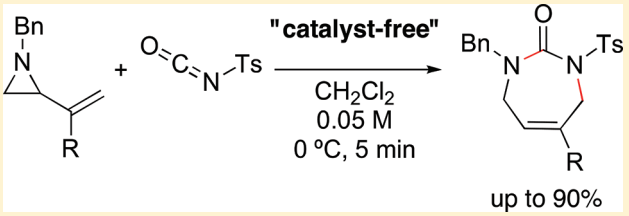
Supporting Information

ABSTRACT: The [5 + 2] cycloaddition reaction of 2-vinylaziridines with sulfonyl isocyanates proceeded smoothly under mild conditions, and various cyclic ureas were isolated in high yields. The remarkable solvent effect on the reaction was observed, and the preferential formation of the seven-membered ring occurred when the reaction was carried out in CH_2Cl_2. The scope and limitation were studied, and the mechanism of this reaction was discussed. This study provides a new and simple method for the synthesis of seven-membered cyclic ureas.



INTRODUCTION

2-Vinylaziridine is a strained and reactive cyclic amine, and many reactions, which involve the cleavage of the C−N bond, have been reported.[1] The formation of seven-membered heterocycles by the intramolecular aza-Cope rearrangement of divinylaziridines[2] and related compounds[3] provided a unique and efficient method for the synthesis of azepane derivatives, and this reaction has been applied to the synthesis of a natural product.[4]

The intermolecular [5 + 2] reaction of vinylaziridines with unsaturated compounds is another attractive approach for the synthesis of the azepane framework, and highly electron-deficient compounds such as hexafluoro-2-butyne[5] or dimethyl acetylenedicarboxylate[6] were employed as the C_2 units.[7] The [5 + 2] reaction of unsubstituted 2-vinylaziridine with phenyl isothiocyanate[8] gave 1,3-thiazepine derivatives, and the formation of a mixture of seven-membered cyclic urea and five-membered heterocycles was reported in the reactions of 2-vinylaziridines with phenyl isocyanate.[9]

We recently reported the ring-expansion reaction ([6 + 2] cycloaddition reaction) of vinylazetidines with electron-deficient isocyanates.[10] The study prompted us to examine the reaction of vinylaziridines with electron-deficient isocyanates. In this paper, we report the [5 + 2] cycloaddition reaction of 2-vinylaziridines and sulfonyl isocyanates.

RESULTS

1-Benzyl-2-vinylaziridine (**1a**) reacted with tosyl isocyanate (**2a**) in the absence of a catalyst, and a mixture of seven-membered and five-membered cyclic ureas was obtained. We studied the effects of the solvent and the concentration on this reaction, and the results are summarized in Table 1.

The cycloaddition reaction proceeded when a 1:1 mixture of the substrates was stirred in acetonitrile at low concentration (0.05 M) overnight (16 h), and a mixture of the seven-membered cyclic urea (**3a**) and five-membered cyclic urea (**4a**) was isolated in 28% combined yield (entry 1). The structure of **3a** was confirmed by X-ray crystallographic analysis (Figure S1, Supporting Information). It is noteworthy that the reaction proceeded in the absence of catalyst, and the seven-membered cyclic urea (**3a**) was isolated as the major product. When we used DMF as the solvent, five-membered cyclic urea (**4a**) was isolated in 51% yield, and the formation of **3a** was not observed (entry 2).[11] The combined yield of the products increased to 58%, and compound **3a** was isolated as the major product when THF was used as the solvent (entry 3). When the reaction was carried out in toluene, the total yield of compounds increased to 62%, and compound **3a** was formed in a highly selective manner (entry 4).

Further studies disclosed that CH_2Cl_2 was the best solvent for this reaction: the combined yield of the product was 64%, and the selective formation of **3a** was observed (entry 5). We studied the effect of the concentration of the substrates on the yields of the products. When the reaction was carried out at higher concentration (0.1 M, or 0.2 M), the yield as well as the selectivity of the products decreased (entries 6 and 7). It also turned out that the reaction proceeded rapidly in CH_2Cl_2: the product was isolated in comparable yield when the reaction time was reduced from 16 h to 5 min (entry 8).

We examined the effect of the temperature on the yield of the products. The reaction proceeded smoothly when the reaction was carried out at 0 °C, and the combined yield of the products reached to 70% (entry 9). On the other hand, the yield decreased when the temperature was set to −20 °C (entry 10).

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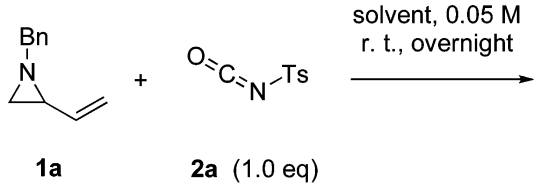
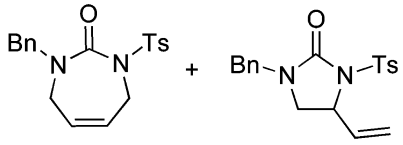
Table 1. Screening of the Reaction Conditions for the [5 + 2] Cycloaddition



1a **2a** (1.0 eq)



3a **4a**

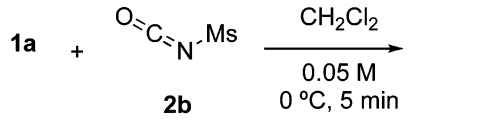
entry	solvent	conc (M)	yield (%)	ratio[a] (3a:4a)
1	CH_3CN	0.05	28	10:1
2	DMF	0.05	51	<5:>95
3	THF	0.05	58	3:1
4	toluene	0.05	62	10:1
5	CH_2Cl_2	0.05	64	>95:<5
6	CH_2Cl_2	0.1	54	10:1
7	CH_2Cl_2	0.2	51	5:1
8[b]	CH_2Cl_2	0.05	65	>95:<5
9[c]	CH_2Cl_2	0.05	70	10:1
10[d]	CH_2Cl_2	0.05	46	10:1

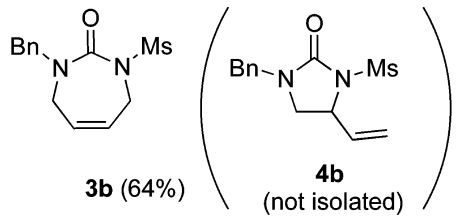
[a]The ratio was estimated by the ^{1}H NMR spectra of the isolated mixture of **3** and **4**. [b]The reaction was carried out for 5 min. [c]The reaction was carried out at 0 °C for 5 min. [d]The reaction was carried out at −20 °C for 5 min.

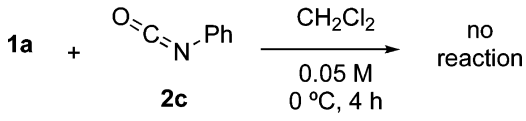
Based on these results, we decided to carry out further studies based on the reaction conditions described in entry 9.

We studied the reaction of **1a** with other isocyanates and found that the sulfonyl isocyanates were suitable substrates for this reaction (Scheme 1). For example, the cycloaddition of **1a** with methanesulfonyl isocyanate (**2b**) proceeded smoothly, and the corresponding seven-membered cyclic urea (**3b**) was isolated in 64% yield. It is noteworthy that the corresponding five-membered cyclic urea was not isolated. On the other hand, phenyl isocyanate (**2c**) was not a good substrate, and the cycloaddition reaction did not proceed when **1a** was treated with **2c** for 4 h at 0 °C.[12] Though the reaction of **1a** with other electron-deficient isocyanates such as trichloroacetyl isocyanate or 4-acetylphenyl isocyanate proceeded, the yields of the products were very low and the purification of the products was difficult.

Scheme 1

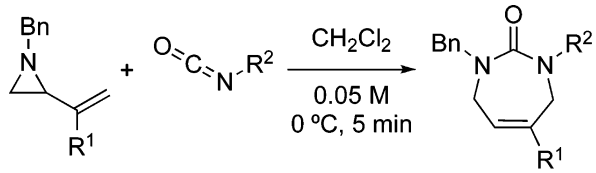






To study the scope and limitation of this reaction, we carried out the reaction of various vinylaziridines with sulfonyl isocyanates. The results of the reactions of substituted 1-benzyl-2-vinylaziridines are summarized in Table 2.

Table 2. [5 + 2] Cycloaddition Reaction of 1-Benzyl-2-vinylaziridines with Sulfonyl Isocyanates



1b-d **2a** (R^2 = Ts) **2b** (R^2 = Ms) **3**

entry	1	R^1	2	yield (%)
1	**1b**	Me	**2a**	82 (**3c**)
2	**1b**	Me	**2b**	89 (**3d**)
3	**1c**	Ph	**2a**	90 (**3e**)
4	**1c**	Ph	**2b**	52 (**3f**)
5	**1d**	OTBS	**2a**	59 (**3g**)
6	**1d**	OTBS	**2b**	48 (**3h**)

As shown in entries 1 and 2, the reaction of 1-benzyl-2-isopropenylaziridine (**1b**) proceeded smoothly with sulfonyl isocyanates, and the corresponding seven-membered ureas were isolated in high yields. The reaction of 1-benzyl-2-(1-phenylvinyl)aziridine (**1c**) with **2a** also proceeded efficiently, and the yield of the product reached to 90% (entry 3). The yield of the product decreased when the reaction of **1c** with **2b** was examined (entry 4). The cyclic ureas were isolated in moderate yields by the reaction of vinylaziridine with OTBS group (**1d**) with **2** (entries 5 and 6). It is noteworthy that the selective formation of the seven-membered urea was observed in these reactions, and a trace amount of five-membered urea was occasionally detected in the crude reaction mixture.

We also examined the reaction of various *N*-substituted vinylaziridines with sulfonyl isocyanates. The results are summarized in Table 3.

The reaction of 1-(2,4-dimethoxybenzyl)-2-vinylaziridine (**1e**) with **2a** as well as **2b** proceeded efficiently, and the corresponding seven-membered cyclic ureas were isolated in good to high yields (entries 1 and 2). 1-Butyl-2-propenylaziridine (**1f**) was a good substrate for this reaction, and the reaction of **1f** with **2a** gave the cyclic urea (**3k**) in 83% yield (entry 3). The reaction of **1f** with **2b** also proceeded smoothly (entry 4). The cycloaddition reaction of 1-cyclohexyl-2-propenylaziridine (**1g**) with **2a** (or **2b**) gave the corresponding cyclic ureas in high yields (entries 5 and 6). It was possible to remove the 2,4-dimethoxybenzyl (DMB) group bound to the cyclic urea under acidic conditions: when compound **3i** was treated with TFA at 60 °C, the deprotected urea (**5**) was isolated in 78% yield (Scheme 2).

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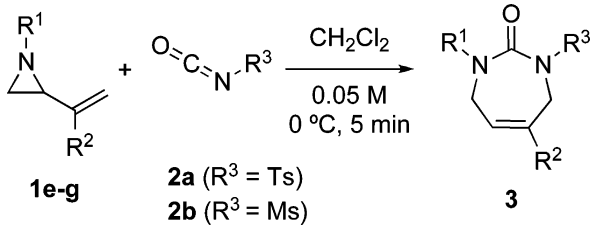
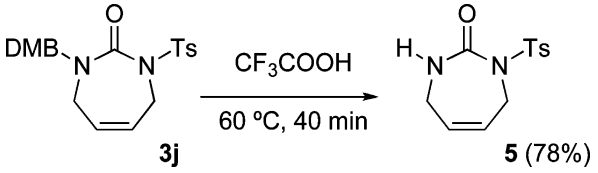
Table 3. [5 + 2] Cycloaddition Reaction of Various Vinylaziridines with Sulfonyl Isocyanates



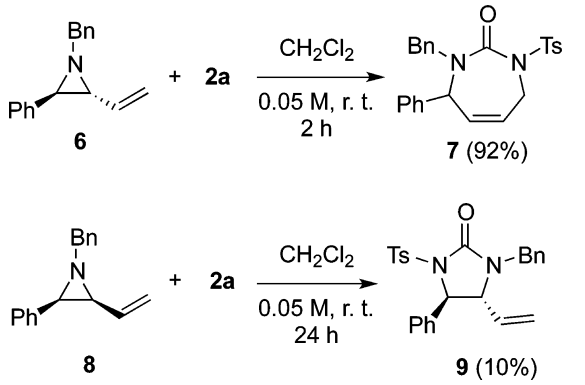
entry	1	R^1	R^2	2	yield (%)
1	**1e**	DMB[a]	H	**2a**	90 (**3i**)
2	**1e**	DMB	H	**2b**	69 (**3j**)
3	**1f**	*n*-Bu	Me	**2a**	83 (**3k**)
4	**1f**	*n*-Bu	Me	**2b**	92 (**3l**)
5	**1g**	Cy[b]	Me	**2a**	92 (**3m**)
6	**1g**	Cy	Me	**2b**	98 (**3n**)

[a]2,4-Dimethoxybenzyl. [b]Cyclohexyl.

Scheme 2. Deprotection of the DMB group



Scheme 3. Cycloaddition Reaction of 1,2,3-Trisubstituted Vinylaziridines with Tosyl Isocyanate (2a)



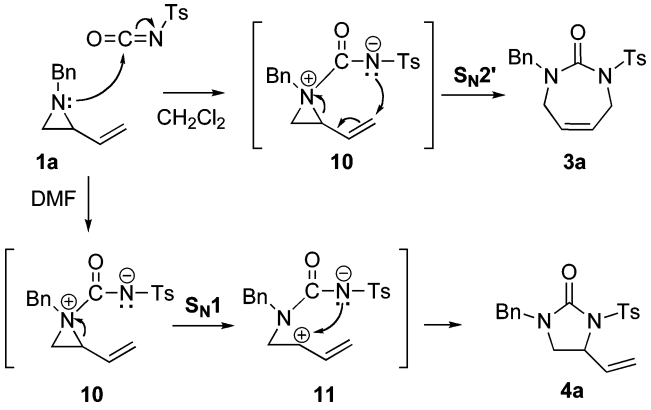
Finally, we studied the reaction of 1,2,3-trisubstituted aziridines with **2a**. The results are summarized in Scheme 3.

The treatment of *trans*-1-benzyl-2-phenyl-3-vinylaziridine (**6**) with **2a** at rt for 2 h gave the corresponding seven-membered cyclic urea (**7**) in 92% yield. On the other hand, the reactivity of the *cis*-vinylaziridine (**8**) was much lower: the progress of the reaction was slow (rt, 24 h), and the five-membered cyclic urea (**9**) was isolated in 10% yield; although we recovered the starting material in low yield (ca. 5%), we could not isolate other products in pure form, and the formation of the seven-membered cyclic urea was not observed.[13] It is noteworthy that the reactivity as well as the pathway of the reaction changed dramatically when a *cis*-vinylaziridine was used as the substrate.

DISCUSSION

In most reactions of 2-vinylaziridine with sulfonyl isocyanates, 2-vinylaziridine reacted as a five-atom unit, and seven-membered cyclic urea was isolated as the major product. We assume that the mechanism of this reaction is similar to the mechanism we discussed in the reaction of 2-vinylazetidines.[10] A plausible mechanism of the reaction is shown in Scheme 4.

Scheme 4. Proposed Mechanism for the Reaction of 2-Vinylaziridine (1a) with Tosyl Isocyanate (2a)



Aziridine **1a** is a good nucleophile and the attack of **1a** toward tosyl isocyanate (**2a**) would proceed to give a zwitterionic species **10** as the key intermediate. The presence of the sulfonyl group would accelerate this process and stabilize the zwitterionic structure. When the intramolecular S_N2' reaction of **10** proceeded, the corresponding seven-membered cyclic urea (**3a**) would be isolated. We previously reported the formation of a small amount of the eight-membered cyclic imine in the reaction of 2-vinylazetidines with **2a**.[10] However, the formation of cyclic imine, which would be formed by the attack of the oxygen atom (instead of the nitrogen atom) to the vinyl group, was not observed in the reaction of 2-vinylaziridines. The zwitterionic species **10** would be more sterically crowded than the zwitterion generated from 2-vinylazetidine, and the tosyl group might be located to the vicinity of the vinyl group, inducing the selective formation of the urea.

When the reaction was carried out in a polar solvent (DMF), the formation of a seven-membered cyclic urea was not observed. In this case, the ring-opening of **10** would give a linear intermediate **11** (or a cationic adduct of the solvent molecule). The five-membered cyclic urea would be formed preferentially by the cyclization reaction of these intermediates.

Remarkable results were observed in the reactions of 1,2,3-trisubstituted vinylaziridines with tosyl isocyanate (**2a**) (Scheme 3). The reaction of the *trans* isomer gave, as expected, the corresponding seven-membered cyclic urea, while the reaction of the *cis* isomer was sluggish and the five-membered cyclic urea was isolated in low yield. These results would be explained in terms of the conformation of the vinylaziridines as well as the structure and reactivity of the corresponding zwitterion (Scheme 5). Since aziridines generally exist as a mixture of invertomers at the aziridine ring nitrogen, the 1,2,3-trisubstituted aziridine would exist as a mixture of nitrogen invertomers such as **A** and **A′**. The ratio and reactivity of the invertomers of the *trans* isomer would be comparable, and two diastereomeric zwitterionic species (**B**, **B′**) would be formed when they reacted with **2a**. Since the vinyl group and the isocyanate group are located at the *cis* position, intermediate **B** would undergo cyclization smoothly, and the seven-membered cyclic urea would be formed. On the other hand, isomer **B′** would not undergo cyclization and the dissociation of the isocyanate would proceed, providing the starting material.

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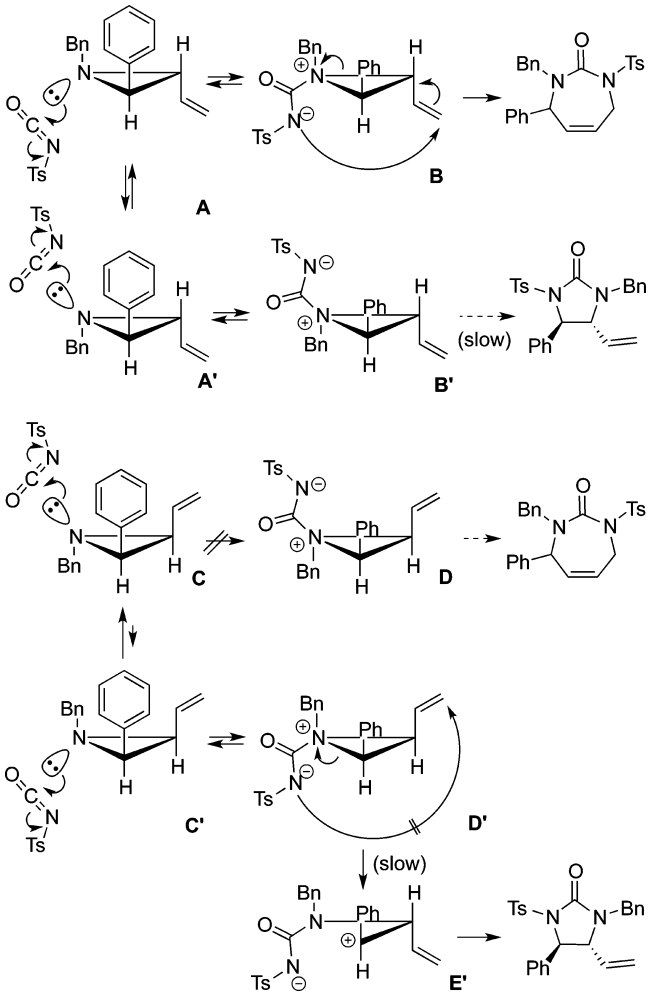
Scheme 5. Proposed Mechanism for the Reaction of Trisubstituted Aziridines with Tosyl Isocyanate (2a)



The stability of the invertomers of the *cis* isomer would be quite different, and invertomer **C** would be the major species. The nucleophilicity of **C**, however, would be very low due to the steric hindrance of the substituents, and the reaction of **C** with the isocyanate would not proceed. The minor invertomer **C**′ would react with isocyanate and intermediate **D**′ would be formed. The rate of the addition reaction would be slow since the concentration of the invertomer **C**′ would be very low. Instead of the cyclization, the simple cleavage of the C−N bond of **D**′ would proceed and a linear intermediate **E**′ would be generated.[14] The five-membered cyclic urea would be formed by the cyclization of **E**′.[15]

CONCLUSION

The [5 + 2] cycloaddition reaction of 2-vinylaziridines with sulfonyl isocyanates proceeded in the absence of catalyst, and the seven-membered cyclic ureas were isolated in good to high yields. Various 2-vinylaziridines turned out to be suitable substrates for this reaction. The use of reactive sulfonyl isocyanates and the choice of CH_2Cl_2 as the solvent are critical for the progress of the reaction. As for the reaction of 1,2,3-trisubstituted aziridines, different products were isolated depending on the structure of the aziridine. The *trans* isomer gave the corresponding seven-membered cyclic urea in high yield. Meanwhile, the reaction of the *cis* isomer proceeded slowly, and the five-membered cyclic urea was isolated in low yield. The mechanism of this reaction was discussed in detail. The study provided a new and simple method for the synthesis of seven-membered cyclic ureas.

EXPERIMENTAL SECTION

General Information. Commercially available reagents were purchased and used without further purification. Aziridine **1a**[16] was prepared by the procedure reported for the preparation of **1e**.[17] Aziridines **1c**[18] and **1e**[17] as well as the isocyanate **2b**[19] were prepared as reported. Chemical shifts were reported in delta units (δ) relative to chloroform (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) or dimethyl sulfoxide (2.49 ppm for ^{1}H NMR and 39.7 ppm for ^{13}C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet).

Preparation of Aziridine 1b. To a mixture of methyltriphenylphosphonium bromide (1.86 g, 5.2 mmol) in THF (20 mL) was added *n*-BuLi (1.6 M in hexane, 3.2 mL, 5.0 mmol), and the mixture was stirred for 30 min. To the yellow mixture was added a solution of 2-acetyl-1-benzylaziridine[20] (910 mg, 3.5 mmol) in THF (5 mL). After being stirred for an additional 21 h at room temperature, the mixture was diluted with diethyl ether, washed with satd NH_4Cl aq, and dried over Na_2SO_4. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10) to yield a yellow oil (426 mg, 72%): ^{1}H NMR (300 MHz, $CDCl_3$) 7.35−7.23 (m, 5 H), 4.96 (dd, J = 0.9, 1.8 Hz, 1 H), 4.83 (d, J = 1.8 Hz, 1 H), 3.63 (d, J = 13.8 Hz, 1 H), 3.35 (d, J = 13.8 Hz, 1 H), 1.98 (dd, J = 3.6, 6.4 Hz, 1 H), 1.90 (d, J = 3.6 Hz, 1 H), 1.62 (d, J = 0.9 Hz, 3 H), 1.52 (d, J = 6.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 143.5, 139.2, 128.2, 127.7, 126.8, 111.6, 64.6, 43.8, 33.7, 18.5; IR (neat) 3028, 2976, 2827, 1644, 1495, 1454, 1356, 1026, 889, 732, 696 cm^{-1}; HR-MS (EI) calcd for $C_{12}H_{15}N$ (M^+) 173.1204, found 173.1206.

Preparation of Aziridine 1d. Triethyamine (0.3 mL, 2.2 mmol) was added to a solution of 2-acetyl-1-benzylaziridine[20] (280 mg, 1.6 mmol) in CH_2Cl_2 (8 mL), and the solution was cooled to 0 °C. TBSOTf (0.45 mL, 1.9 mmol) was added over 5 min, and the mixture was stirred at 0 °C for 1 h. The reaction was quenched with brine and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:20) to yield a colorless oil (305 mg, 66%): ^{1}H NMR (300 MHz, $CDCl_3$) 7.36−7.22 (m, 5 H), 4.33 (s, 1 H), 4.15 (s, 1 H), 3.47 (s, 2 H), 1.92 (dd, J = 3.4, 6.0 Hz, 1 H), 1.89 (d, J = 3.4 Hz, 1 H), 1.47 (d, J = 6.0 Hz, 1 H), 0.90 (s, 9 H), 0.13 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) 156.8, 139.1, 128.2, 127.8, 126.8, 91.2, 64.4, 41.4, 34.0, 25.7, 18.1, −4.67, −4.72; IR (neat) 2930, 2857, 1636, 1472, 1361, 1294, 1251, 1028, 838, 781, 731, 696 cm^{-1}. Anal. Calcd for $C_{17}H_{27}NOSi$: C, 70.53; H, 9.40; N, 4.84. Found: C, 70.25; H, 9.49; N, 4.80.

Preparation of Aziridine 1f. To a solution of 1,2-dibromobutan-3-one[21] (3.4 g, 15 mmol) in THF (50 mL) was added *n*-butylamine (1.63 mL, 16.5 mmol) at 0 °C. After 5 min, DBU (4.5 mL, 30 mmol) was added and the mixture was stirred at ambient temperature for overnight. The salt was filtered off and the solid was rinsed with diethyl ether. The combined filtrate was evaporated and purified by silica gel column chromatography (ethyl acetate/hexane = 1:5) to afford 2-acetyl-1-*n*-butylaziridine (1.44 g, 69%) as a brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) 2.31−2.36 (m, 1 H), 2.20−2.24 (m, 1 H), 2.07 (m, 1 H), 2.00 (s, 3 H), 1.99 (m, 1 H), 1.59 (d, J = 6.4 Hz, 1 H), 1.49−1.54 (m, 2 H), 1.32−1.36 (m, 2 H), 0.89 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) 207.7, 60.6, 45.3, 35.0, 31.6, 24.9, 20.4, 14.0; IR (neat) 3394, 3047, 2954, 2931, 2870, 1705, 1466, 1427, 1358, 1257, 1211, 1173, 1088, 1026, 972, 918, 787, 517 cm^{-1}; HR-MS (EI) calcd for $C_8H_{14}NO$ ([M + H]$^+$) 140.1070, found 140.1075.

To a solution of methyltriphenylphosphonium bromide (5.5 g, 15.4 mmol) in THF (40 mL) was added *n*-BuLi (1.6 M in hexanes, 9.7 mL, 15.4 mmol) at 0 °C, and the mixture was stirred for 30 min. A solution of 2-acetyl-1-butylaziridine (1.45 g, 10.3 mmol) in THF (10 mL) was added, and the mixture was warmed to room temperature and stirred

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for 13 h. The reaction mixture was diluted with diethyl ether, washed with satd NH_4Cl aq, and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10). The product **1f** was obtained as a colorless oil (730 mg, 50%): ^{1}H NMR (300 MHz, $CDCl_3$) 4.94 (s, 1 H), 4.81(m, 1 H), 2.43(m, 1 H), 2.08 (m, 1 H), 1.77 (m, 1 H), 1.63 (m, 2 H), 1.58−0.87 (m, 10 H); ^{13}C NMR (150 MHz, $CDCl_3$) 144.0, 111.3, 61.4, 43.7, 33.6, 31.9, 20.5, 18.7, 14.1; IR (neat) 2959, 2931, 2811, 1644, 1455, 1376, 1236, 1084, 882 cm^{-1}; HR-MS (EI$^+$) calcd for $C_9H_{16}N$ ([M − H]$^+$) 138.1283, found 138.1284.

Preparation of Aziridine 1g. To the solution of 1,2-dibromobutan-3-one[21] (3.4 g, 15 mmol) in THF (50 mL) was added cyclohexylamine (1.9 mL, 16.5 mmol) at 0 °C. After 5 min, DBU (4.5 mL, 30 mmol) was added, and the mixture was stirred at ambient temperature overnight. The salt was filtered off and washed with diethyl ether. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:5) to afford 2-acetyl-1-cyclohexylaziridine (1.68 g, 66%) as a pale brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) 2.03 (m, 1 H), 2.01 (s, 3 H), 1.73 (m, 4 H), 1.61 (d, J = 6.8 Hz, 1 H), 1.54 (m, 1 H), 1.32−1.40 (m, 2 H), 1.12−1.20 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) 207.8, 68.7, 44.2, 33.8, 32.5, 32.4, 26.0, 25.2, 24.51, 24.45; IR (neat) 3047, 2978, 2931, 2854, 1705, 1450, 1358, 1257, 1219, 1165, 1088, 1034, 980 cm^{-1}; HR-MS (EI) calcd for $C_{10}H_{17}NO$ (M$^+$) 167.1310, found 167.1306.

To a mixture of methyltriphenylphosphonium bromide (5.4 g, 15.1 mmol) in THF (50 mL) was added *n*-BuLi (1.6 M in hexane, 9.1 mL, 15.1 mmol) at 0 °C. To the solution was added 2-acetyl-1-cyclohexylaziridine (1.68 g, 10.0 mmol) in THF (10 mL), and the mixture was stirred for 5 h at room temperature. The solution was diluted with diethyl ether, washed with satd NH_4Cl aq, and dried over Na_2SO_4. The solvent was removed in vacuo, and the crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1:10) to afford **1g** as a colorless oil (1.31 g, 79%): ^{1}H NMR (300 MHz, $CDCl_3$) 4.91 (m, 1 H), 4.80 (m, 1 H), 1.81−1.06 (m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.1, 111.2, 69.5, 42.4, 32.9, 32.23, 32.18, 26.1, 24.82, 24.79, 19.3; IR (neat) 2972, 2928, 2854, 1643, 1450, 1368, 1226, 1167, 881, 829 cm^{-1}; HR-MS (EI) calcd for $C_{11}H_{19}N$ (M$^+$) 165.1517, found 165.1513.

General Procedure for the Cycloaddition of Vinylaziridines and Sulfonyl Isocyanates. To a solution of sulfonyl isocyanate (0.5 mmol) in CH_2Cl_2 (9 mL) was added vinylaziridine (0.5 mmol) in CH_2Cl_2 (1 mL) and the solution stirred at the designated temperature. The progress of the reaction was monitored by TLC and/or GC−MS. After the consumption of vinylaziridine, the solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate) to give the product.

3a: colorless solid; mp 227.5−231.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.98−7.20 (m, 9 H), 5.71 (m, 1 H), 5.66 (m, 1 H), 4.54 (s, 2 H), 4.09 (s, 2 H), 3.89 (s, 2 H), 2.42 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) 157.7, 144.1, 136.0, 135.8, 129.3, 128.71, 128.69, 127.70, 127.68, 126.1, 124.9, 52.6, 46.9, 45.5, 21.6; IR (KBr) 3035, 1698, 1472, 1455, 1431, 1348, 1239, 1159, 1095, 876, 819, 735, 666, 589, 539 cm^{-1}. Anal. Calcd for $C_{19}H_{20}N_2O_3S$: C, 64.02; H, 5.66; N, 7.86. Found: C, 63.84; H, 5.73; N, 7.82.

3b: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.34−7.23 (m, 5 H), 5.74−5.71 (m, 1 H), 5.69−5.66 (m, 1 H), 4.57 (s, 2 H), 4.20−4.18 (m, 2 H), 3.88−3.86 (m, 2 H), 3.26 (s, 3 H); ^{13}C NMR(75 MHz, $CDCl_3$) 158.3, 135.9, 128.8, 127.8, 127.7, 126.0, 124.9, 52.8, 46.7, 45.7, 39.8; IR (KBr) 3626, 3033, 2930, 1691, 1496, 1471, 1421, 1343, 1239, 1159, 1092, 1029, 965, 933, 878, 762, 700, 557, 514, 468 cm^{-1}; HR-MS (ESI) calcd for $C_{13}H_{16}N_2O_3SNa$ ([M + Na]$^+$) 303.0774, found 303.0765.

3c: colorless solid; mp 165−166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.99−7.20 (m 9 H), 5.46 (d, J = 1.5 Hz, 1 H), 4.52 (s, 2 H), 3.90 (s, 2 H), 3.82 (d, J = 4.3 Hz, 2 H), 2.42 (s, 3 H), 1.64 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) 157.5, 144.1, 136.1, 135.8, 133.9, 129.4, 128.8, 128.7, 127.69, 127.66, 119.6, 52.3, 50.2, 45.1, 21.6, 21.0; IR (KBr) 2913, 1683, 1473, 1449, 1428, 1347, 1231, 1161, 748, 733, 704, 689, 542 cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56. Found: C, 64.55; H, 5.99; N, 7.44.

3d: colorless solid; mp 122.0−123.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.35−7.22 (m, 5 H), 5.47 (m, 1 H), 4.55 (s, 2 H), 4.02 (m, 2 H), 3.80 (m, 2 H), 3.27 (m, 3 H), 1.67 (d, J = 1.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 158.0, 135.9, 133.8, 128.8, 127.8, 127.7, 119.5, 52.4, 50.1, 45.3, 39.7, 21.0; IR (KBr) 3005, 2925, 1681, 1605, 1476, 1455, 1424, 1335, 1262, 1149, 1109, 1062, 1003, 963, 929, 795, 773, 729, 696, 517 cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_2O_3S$: C, 57.12; H, 6.16; N, 9.52. Found: C, 57.18, H, 6.35, N, 9.35.

3e: colorless amorphous; ^{1}H NMR (300 MHz, $CDCl_3$) 8.02−7.19 (m, 14 H), 5.82 (m, 1 H), 4.58 (s, 2 H), 4.39 (d, J = 2.1 Hz, 2 H), 4.04 (m, 2 H), 2.42 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.6, 144.2, 139.1, 138.0, 136.1, 135.9, 129.4, 128.8, 127.77, 128.76, 128.6, 128.2, 127.8, 126.2, 122.6, 52.5, 49.2, 45.9, 21.6; IR (neat) 3735, 3648, 1698, 1472, 1351, 1228, 1163, 1099, 741, 698, 659, 598, 574 cm^{-1}. Anal. Calcd for $C_{25}H_{24}N_2O_3S$: C, 69.42; H, 5.59; N, 6.48. Found: C, 69.17; H, 5.89; N, 6.34.

3f: colorless solid; mp 131−132.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.37−7.20 (m, 10 H), 5.85 (tt, J = 5.5, 1.7 Hz, 1 H), 4.62 (s, 2 H), 4.50 (q, J = 2.1 Hz, 2 H), 4.02 (dt, J = 5.5, 2.1 Hz, 2 H), 3.32 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 187.1, 138.8, 137.8, 135.9, 128.8, 128.7, 128.4, 127.9, 127.8, 126.2, 122.4, 52.6, 49.0, 46.0, 40.0; IR (KBr) 3026, 2924, 2360, 1698, 1468, 1335, 1159, 966, 765, 696, 497 cm^{-1}; HR-MS (ESI) calcd for $C_{19}H_{20}N_2O_3S$ ([M + Na]$^+$) 379.1087, found 379.1099.

3g: colorless solid; mp 127.8−130.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.96 (d, J = 8.4 Hz, 2H), 7.34−7.21 (m, 7 H), 4.89 (t, J = 6.0 Hz, 1 H), 4.53 (s, 2 H), 3.86 (d, J = 1.5 Hz, 2 H), 3.82 (d, 6.0 Hz, 2 H), 2.42 (s, 3 H), 0.86 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) 156.9, 149.5, 144.1, 136.1, 135.8, 129.4, 128.73, 128.70, 127.8, 127.7, 101.6, 52.3, 48.8, 43.3, 25.5, 21.6, 17.9, −4.7; IR (KBr) 3648, 2929, 1696, 1464, 1350, 1244, 1210, 1166, 1099, 884, 830, 733, 664, 592, 546, 507 cm^{-1}. Anal. Calcd for $C_{25}H_{34}N_2O_4SSi$: C, 61.69; H, 7.04; N, 5.76. Found: C, 61.66; H, 7.16; N, 5.61.

3h: colorless solid; mp 79−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.34−7.26 (m, 5 H), 4.91 (t, J = 5.5 Hz, 1 H), 4.57 (s, 2 H), 3.97 (s, 2 H), 3.80 (d, J = 5.7 Hz, 2 H), 3.27 (s, 3 H), 0.88 (s, 9 H), 0.08 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.5, 149.3, 135.9, 128.8, 127.8, 127.7, 101.4, 52.3, 48.8, 43.4, 39.8, 25.4, 17.9, −4.7; IR (KBr) 3029, 2931, 2858, 1687, 1469, 1427, 1342, 1283, 1247, 1198, 1130, 1097, 1079, 1050, 1008, 965, 934, 886, 843, 777, 737, 698, 639, 590, 556, 515, 490 cm^{-1}; HR-MS (ESI) calcd for $C_{19}H_{30}N_2O_4SSi$ ([M + Na]$^+$) 433.1588, found 433.1583.

3i: colorless solid; mp 143−144.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.96 (d, J = 8.3 Hz, 2 H), 7.30 (d, J = 8.1 Hz, 2 H), 7.11 (d, J = 8.1 Hz, 1 H), 6.40 (m, 2 H), 5.66 (m, 1 H), 5.56 (m, 1 H), 4.47 (s, 2 H), 4.02 (m, 2 H), 3.91 (m, 2 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.6, 158.5, 157.2, 143.9, 136.0, 130.4, 129.3, 128.7, 125.8, 125.2, 116.7, 104.1, 98.4, 55.3, 55.2, 47.2, 46.9, 45.3, 21.6; IR (KBr) 2935, 1695, 1614, 1508, 1465, 1417, 1349, 1290, 1209, 1162, 1124, 1092, 1035, 876, 815, 739, 665, 588, 549 cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_2O_5S$: C, 60.56; H, 5.81; N, 6.73. Found: C, 60.39; H, 5.91; N, 6.68.

3j: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.13 (d, J = 7.9, 1 H) 6.45−6.41 (m, 2 H), 5.69−5.65 (m, 1 H), 5.59−5.56 (m, 1 H), 4.50 (s, 2 H), 4.12 (s, 2 H), 3.90 (s, 2 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 3.24 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.0, 158.5, 157.7, 130.6, 125.5, 125.2, 116.5, 104.1, 98.4, 55.4, 55.3, 47.5, 46.7, 45.4, 39.7; IR (KBr) 3628, 2936, 2839, 1696, 1613, 1508, 1340, 1160, 1085, 1035, 966, 878, 835, 761, 735, 703, 645, 568, 535, 512 cm^{-1}; HR-MS (ESI) calcd for $C_{15}H_{20}N_2O_5S$ ([M + Na]$^+$) 363.0985, found 363.0974.

3k: colorless solid; mp 147.5−149.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.94 (d, J = 8.2 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 5.60 (m, 1 H), 3.90 (d, J = 4.3 Hz, 1 H), 3.83 (s, 3 H), 3.30 (t, J = 7.5 Hz, 2 H), 2.41 (s, 3 H), 1.65 (s, 3 H), 1.51−0.84 (m, 7 H); ^{13}C NMR (150 MHz, $CDCl_3$) 156.5, 143.9, 135.8, 134.1, 129.3, 128.7, 119.8, 50.2, 49.1, 45.6, 30.0, 21.6, 21.0, 19.9, 13.8; IR (KBr) 2963, 2859, 1698, 1473, 1340, 1238, 1159, 1103, 1035, 832, 746, 657, 580, 542, 513 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_3S$: C, 60.69; H, 7.19; N, 8.33. Found: C, 60.55; H, 7.17; N, 8.22.

3l: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 5.60 (m, 1 H), 3.95 (d, J = 0.9 Hz, 2 H), 3.86 (m, 2 H), 3.34 (t, J = 7.2 Hz, 2 H), 3.22 (s, 3 H), 1.68 (d, J = 1.1 Hz, 3 H), 1.48 (m, 2 H), 1.32 (m, 2 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.2, 133.9, 119.7, 50.1, 49.0, 45.6, 39.5, 30.0, 21.0, 19.9, 13.8; IR (KBr) 3386, 2931, 2870, 1689, 1473, 1427, 1342, 1234, 1157, 1118, 1034, 1003, 964, 833, 764, 555, 517 cm^{-1}. Anal. Calcd for $C_{11}H_{20}N_2O_3S$: C, 50.75; H, 7.74; N, 10.76. Found: C, 50.95, H, 7.72, N, 10.80.

3m: colorless solid; mp 227.5−231.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.94 (d, J = 8.2 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 5.57 (br, 1 H), 4.02 (br, 1 H), 3.84 (br, 4 H), 2.41 (s, 3 H), 1.74−1.01 (br, 13 H); ^{13}C NMR (75 MHz, $CDCl_3$) 156.7, 143.9, 135.8, 134.0, 129.2, 128.8, 120.5, 55.2, 50.4, 39.4, 30.5, 25.5, 25.3, 21.6, 21.0; IR (KBr) 2929, 2857, 1684, 1471, 1342, 1243, 1162, 1032, 894, 818, 741, 657, 582, 545 cm^{-1}. Anal. Calcd for $C_{19}H_{26}N_2O_3S$: C, 62.96; H, 7.23; N, 7.73. Found: C, 62.83; H, 7.31; N, 7.58.

3n: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 5.59−5.55 (m, 1 H), 4.09−4.00 (m, 1 H), 3.95 (d, J = 0.8 Hz, 2 H), 3.80 (dd, J = 5.7, 1.1 Hz, 2 H), 3.22 (s, 3 H), 1.75−1.03 (m, 13 H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.2, 133.9, 120.4, 55.4, 50.2, 39.5, 39.4, 30.5, 25.4, 25.3, 20.9; IR(KBr) 3410, 2932, 2857, 1683, 1470, 1345, 1243, 1156, 1057, 1037, 1006, 967, 897, 759, 692, 650, 563, 522; HR-MS (ESI) calcd for $C_{13}H_{22}N_2O_3SNa$ ([M + Na]$^+$) 309.1243, found 309.1244.

4a: colorless solid; mp 91.4−93.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.94−7.11 (m, 9 H), 5.76 (ddd, J = 7.9, 10.2, 17.0 Hz, 1 H), 5.35 (d, J = 17.0 Hz, 1 H), 5.23 (d, J = 10.2 Hz, 1 H), 4.70 (m, 1 H), 4.34 (d, J = 14.9 Hz, 1 H), 4.27 (d, J = 14.9 Hz, 1 H), 3.45 (dd, J = 4.5, 9.1 Hz, 1 H), 2.90 (dd, J = 3.6, 9.1 Hz, 1 H), 2.42 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 153.5, 144.4, 136.2, 135.19, 135.17, 129.3, 128.7, 128.3, 128.0, 127.8, 118.6, 56.3, 47.8, 47.5, 21.5; IR (KBr) 2926, 1723, 1493, 1420, 1363, 1174, 1092, 942, 813, 758, 705, 663, 584, 547 cm^{-1}. Anal. Calcd for $C_{19}H_{20}N_2O_3S$: C, 64.02; H, 5.66; N, 7.86. Found: C, 64.30; H, 5.76; N, 7.83.

Synthesis of 5 by the Deprotection of 3j. Compound **3j** (208 mg, 0.50 mmol) was dissolved with TFA (5 mL), and the mixture was stirred for 40 min at 60 °C. The reaction was quenched by addition of saturated $NaHCO_3$ aq, and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 1:2) to afford **5** as colorless solid (102 mg, 78%): mp 160.5−163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.93 (d, J = 8.3 Hz, 2 H), 7.30 (d, J = 7.9 Hz, 2 H), 5.75 (m, 2 H), 5.18 (brs, 1 H), 4.10 (d, J = 2.4 Hz, 2 H), 3.85 (t, J = 4.1 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 195.8, 158.8, 144.2, 129.4, 128.7, 125.5, 125.4, 46.1, 41.0, 21.6; IR (KBr) 3304, 1714, 1666, 1462, 1347, 1162, 1115, 1091, 909, 812, 674, 623, 571, 536, 450, 408 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_3S$: C, 54.12; H, 5.30; N, 10.52. Found: C, 54.41; H, 5.25; N, 10.43.

Preparation of 6 and 8. General Procedure. DIBAL-H (1.04 M in hexane, 20.2 mL, 21 mmol) was added dropwise to a stirred solution of *cis*(or *trans*)-1-benzyl-2-methoxycarbonyl-3-phenylaziridine[21] (3.04 g, 14 mmol) in CH_2Cl_2 (42 mL) at −78 °C. After 100 min, Na_2SO_4·10H_2O (5 g) was added and the reaction mixture allowed to reach rt. The inorganic precipitate was filtered off and washed with ethyl acetate. The filtrate was dried (Na_2SO_4) and the solvent removed in vacuo. The crude aldehyde was unstable, and it was used for the next step without further purification. To a mixture of methyltriphenylphosphonium bromide (7.5 g, 21 mmol) in THF (75 mL) was added *n*-BuLi (1.6 M in hexane, 12.7 mL, 21 mmol) at 0 °C, and the mixture was stirred for 30 min. A solution of aldehyde (2.2 mmol) in THF (3 mL) was added. The mixture was warmed to room temperature and stirred for additional 15 h. The solution was diluted with ethyl ether, and the combined organic layer was washed with water and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (ethyl acetate/hexane).

6: yield 59%; yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.41−7.17 (m, 10 H), 5.95 (dt, J = 17.0, 9.6 Hz, 1 H), 6.43 (d, J = 17.0 Hz, 1 H), 5.33 (d, J = 10.2 Hz, 1 H), 4.00 (d, J = 14.3 Hz, 1 H), 3.78 (d, J = 14.1 Hz, 1 H), 2.73 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) 139.7, 139.6, 132.6, 128.3, 128.2, 127.6, 126.9, 126.7, 126.1, 120.5, 56.7, 50.2, 49.2; IR (KBr) 3032, 2985, 2846, 1951, 1882, 1736, 1604, 1496, 1450, 1358, 1242, 1103, 1026, 987, 918, 810, 733, 694, 609, 532, 463 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.62; H, 7.30; N, 6.10.

8: yield 47%; pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 7.97 (m, 10 H), 5.26−5.43 (m, 2 H), 5.04−5.08 (m, 1 H), 3.86 (d, J = 13.6 Hz, 1 H), 3.62 (d, J = 13.6 Hz, 1 H), 2.89 (d, J = 6.4 Hz, 1 H), 2.41 (t, J = 7.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) 139.0, 137.0, 134.6, 128.3, 127.9, 127.8, 127.7, 126.9, 126.7, 118.1, 64.2, 48.9, 48.0; IR (KBr) 3062, 3032, 2985, 2954, 2924, 2823, 1635, 1604, 1496, 1450, 1389, 1358, 1304, 1250, 1196, 1165, 1103, 1072, 1026, 987, 918, 841, 741, 702, 602, 463 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.26; N, 5.95. Found: C, 86.52; H, 7.26; N, 5.82.

7: colorless amorphous solid; ^{1}H NMR (300 MHz, $CDCl_3$) 7.88 (d, J = 8.3 Hz, 2 H), 7.36−7.20 (m, 12 H), 6.00−5.79 (m, 1 H), 5.86−5.79 (m, 1 H), 5.14 (d, J = 15.1 Hz, 1 H), 4.83 (d, J = 6.6 Hz, 1 H), 4.48 (dd, J = 17.1, 6.0 Hz, 1 H), 4.12 (d, J = 15.4 Hz, 1 H), 3.93 (dq, J = 17.3, 2.4 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 157.9, 144.1, 138.5, 136.5, 136.2, 129.3, 129.0, 128.8, 128.7, 128.6, 128.2, 128.0, 127.7, 126.5, 125.1, 61.6, 52.7, 45.9, 21.6; IR (KBr) 3033, 1685, 1598, 1439, 1357, 1306, 1244, 1167, 1096, 1031, 872, 819, 733, 665, 592, 545, 509, 457 cm^{-1}; HR-MS (ESI) calcd for $C_{25}H_{24}N_2O_3SNa$ ([M + Na]$^+$) 455.1400, found 455.1403.

9: colorless amorphous solid; ^{1}H NMR (300 MHz, $CDCl_3$) 7.53 (d, J = 8.3, 2 H), 7.30−7.12 (m, 10 H), 7.02 (d, J = 7.2 Hz, 2 H), 5.30 (d, J = 8.7 Hz, 1 H), 5.16 (dd, J = 9.6, 1.1 Hz, 1 H), 5.11 (d, J = 2.3 Hz, 1 H), 4.94 (dt, J = 16.4, 9.4 Hz, 1 H), 4.77 (d, J = 14.9 Hz, 1 H), 4.25 (t, J = 8.9 Hz, 1 H), 3.88 (d, J = 15.1 Hz, 1 H), 2.40 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 156.9, 144.3, 136.0, 135.5, 135.0, 132.2, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 122.8, 61.9, 61.3, 45.4 21.6; IR (KBr) 3425, 1720, 1496, 1458, 1412, 1358, 1288, 1250, 1211, 1273, 1134, 1095, 1026, 810, 756, 702, 663, 579, 540 cm^{-1}; HR-MS (ESI) calcd for $C_{25}H_{24}N_2O_3SNa$ ([M + Na]$^+$) 455.1400, found 455.1418.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for **3a** (CIF). Crystal structure of **3a** and NMR spectra (^{1}H, ^{13}C) for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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