# An Efficient Method for Opening *N*-Tosylaziridines with Silylated Nucleophiles by Using Polystyrene-Supported 1,5,7-Triazabicyclo[4.4.0]dec-5-ene as a Reusable Organocatalyst

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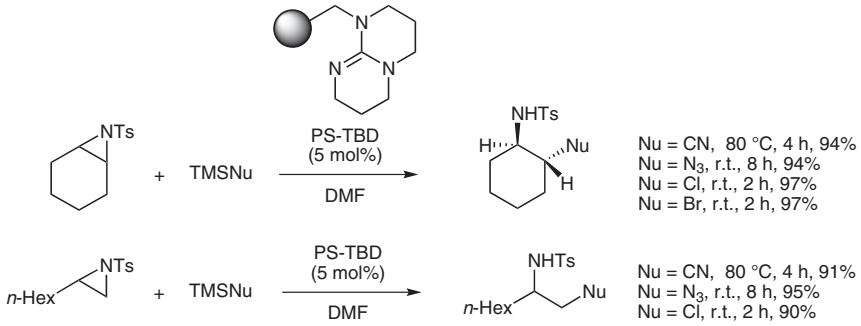
**Abstract:** Polystyrene-supported 1,5,7-triazabicyclo[4.4.0]dec-5-ene (PS-TBD) catalyzes the ring opening of *N*-tosylaziridines with trimethylsilyl cyanide, trimethylsilyl azide, or trimethylsilyl halides to give the corresponding products in high yields. PS-TBD can be easily recovered and reused without significant loss of catalytic activity.

**Keywords:** catalysis, polymers, ring opening, heterocycles, aziridines, sulfonamides




**Scheme 1** Ring opening of *N*-tosylaziridines catalyzed by PS-TBD

Aziridines, as small-ring heterocycles, are very useful intermediates for the synthesis of many nitrogen-containing biologically active compounds.[1] Consequently, numerous ring-opening reactions of activated or nonactivated aziridines have been reported.[2] Among these approaches, ring cleavage with silylated nucleophiles, such as silyl cyanides, azides, or halides, is an important reaction for the preparation of highly functionalized compounds. Ring-opening reactions with silylated nucleophiles catalyzed by Lewis acids,[3] fluoride ion,[4] Lewis bases,[5] or N-heterocyclic carbenes[6] have been developed to realize high yields and high selectivities. In search of a broadly applicable and environmentally friendly reaction, we planned to use a polymer-supported organobase as a recyclable Lewis base catalyst.

Polymer-supported catalysts have attracted considerable attention in recent decades because of their inherent advantages in synthetic chemistry; these include simplification of reaction procedures, easy recovery of the catalyst by filtration, applicability in automated systems, and reusability.[7] 1,5,7-Triazabicyclo[4,4,0]dec-5-ene functionalized polystyrene (PS-TBD) is a polymer-supported organobase catalyst that consists of a bicyclic guanidine moiety {1,5,7-triazabicyclo[4.4.0]dec-5-ene (1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine)} anchored on polystyrene. This catalyst has been used to mediate the alkylation of phenols, amines, active methylene compounds, and thiols; the esterification of carboxylic acids; the dehalogenation of organic halides; and the high-throughput syntheses of aryl triflates and aryl nonaflates.[8] PS-TBD is also a good catalyst for the Henry reaction and for the addition of dialkyl phosphites to a variety of carbonyl compounds and imines.[9] Recently, PS-TBD catalyzed ring-opening reactions of epoxides, aldol-type condensations, and Michael additions have also been reported.[10] We have reported the use of PS-TBD as a base catalyst for the cyanosilylation of carbonyl compounds and imines.[11] Here, we present a practical procedure for ring cleavage of aziridines with silylated nucleophiles by using polystyrene-supported TBD as a reusable organocatalyst (Scheme 1).[12]

First, we examined the ring-opening reaction of 7-tosyl-7-azabicyclo[4.1.0]heptane (**1a**) with trimethylsilyl cyanide in the presence of 5 mol% of PS-TBD in *N*,*N*-dimethylformamide at 80 °C. The desired sulfonamide **2a** was ob-

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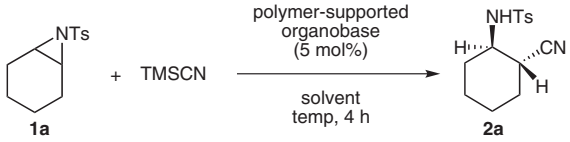
tained in 95% yield after four hours. The catalytic activities of polystyrene-supported 4-(*N*,*N*-dimethylamino)pyridine (PS-DMAP), triphenylphosphine (PS-$PPh_3$), and *N*,*N*-diisopropylethylamine (PS-DIPEA) were inferior to those of PS-TBD (Table 1, entries 1, 3, 4 and 5; Figure 1). Product **2a** was obtained in a low yield when other solvents such as tetrahydrofuran, dichloromethane, acetonitrile, or toluene were used (entries 3–5). We also examined the reaction in under solvent-free conditions (entry 6), but the yield was unsatisfactory because *N*-tosylaziridine is a solid substrate and is difficult to mix without a solvent.

**Table 1** Optimization of the Reaction Conditions




| Entry | Base | Solvent | Temp (°C) | Yield (%) |
|---|---|---|---|---|
| 1 | PS-TBD | DMF | 80 °C | 95 |
| 2 | PS-TBD | DMF | r.t. | 11 |
| 3 | PS-DMAP | DMF | 80 °C | 45 |
| 4 | PS-$PPh_3$ | DMF | 80 °C | 51 |
| 5 | PS-DIPEA | DMF | 80 °C | 12 |
| 6 | PS-TBD | THF | 66 °C (reflux) | trace |
| 7 | PS-TBD | MeCN | 82 °C (reflux) | 15 |
| 8 | PS-TBD | $CH_2Cl_2$ | 40 °C (reflux) | trace |
| 9 | PS-TBD | toluene | 80 °C | trace |
| 10 | PS-TBD | – | 80 °C | 48 |

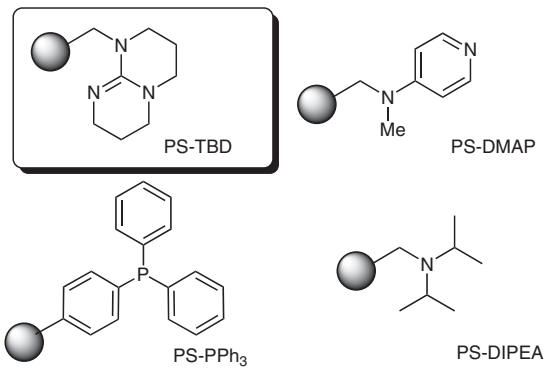
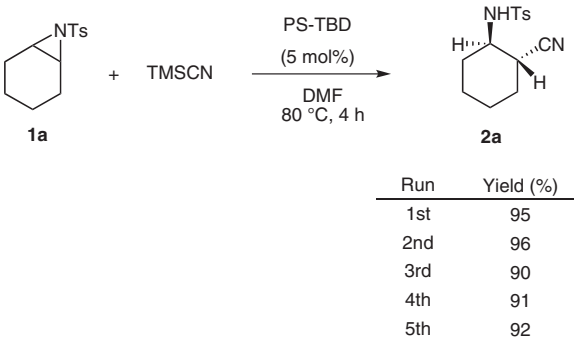



**Figure 1**

We then examined the recovery and reuse of PS-TBD in the reaction of aziridine **1a** with trimethylsilyl cyanide (Scheme 2). When the reaction was completed, ethyl acetate was added to the reaction mixture and the catalyst was recovered by filtration. The recovered catalyst was



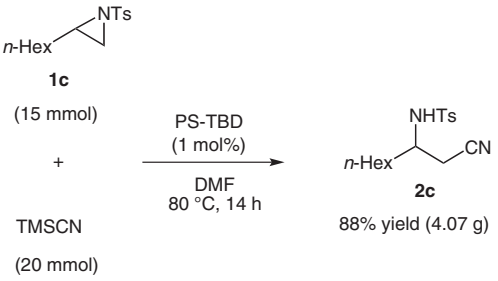

| Run | Yield (%) |
|---|---|
| 1st | 95 |
| 2nd | 96 |
| 3rd | 90 |
| 4th | 91 |
| 5th | 92 |

**Scheme 2** Reuse of recovered PS-TBD

washed, dried, and reused. The catalyst retained its catalytic activity after four further runs.

To clarify the scope of this reaction, we examined the reactions of several *N*-tosylaziridines in the presence of 5 mol% PS-TBD (Table 2). The ring-opening reactions of both 2-substituted *N*-tosylaziridines and 2,3-disubstituted *N*-tosylaziridines all occurred smoothly to afford the corresponding products in good to excellent yields. In the case of 2-substituted *N*-tosylaziridines, the reaction proceeded smoothly when 1 mol% of PS-TBD was used. Almost complete regioselectivity (> 98:2) was observed with both phenyl- and alkyl-substituted *N*-tosylaziridines. Unfortunately, in the case of the less-reactive *trans*-2,3-diphenyl-1-tosylaziridine (**1i**), the yield was unsatisfactory.

A gram-scale synthesis of the ring-opening reaction of *N*-tosylaziridine **1c** with trimethylsilyl cyanide was performed to examine the synthetic potential of the reaction. In the presence of 1 mol% of PS-TBD, 15 mmol of *N*-tosylaziridine **1c** reacted with 20 mmol of trimethylsilyl cyanide to give the corresponding product **2c** in 88% yield (Scheme 3).



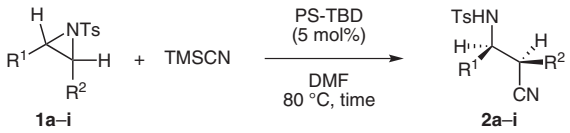

**Scheme 3** Scaled-up version of the ring-opening reaction

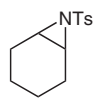
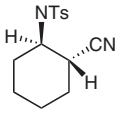
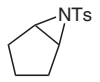
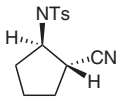
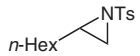
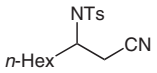
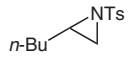
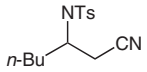
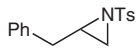
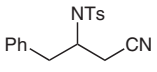
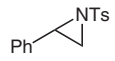
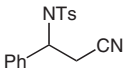
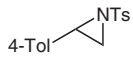
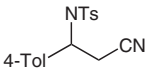
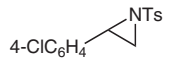
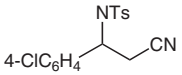
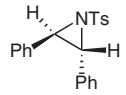
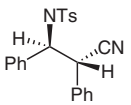
We found that the TBD-catalyzed reaction was also applicable to other silylated nucleophiles: trimethylsilyl azide and trimethylsilyl halides (Table 3). The reaction proceeded smoothly at room temperature to give the corresponding products in high yields from both 2-substituted aziridines and 2,3-disubstituted aziridines. In this case, the less-reactive 2,3-diphenylaziridine **1i** also gave good results. A high level of regioselectivity (>95:5) was ob-



**Table 2** PS-TBD-Catalyzed Ring-Opening Reactions of Various Aziridines with Trimethylsilyl Cyanide

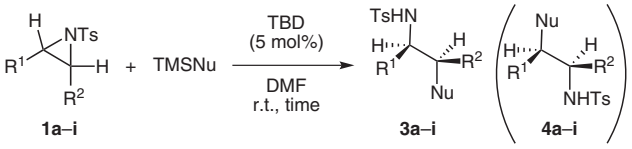



| Entry | Aziridine | Product | Time (h) | Yield[a] (%) |
|---|---|---|---|---|
| 1 |  **1a** |  **2a** | 4 | 85 |
| 2 |  **1b** |  **2b** | 12 | 89 |
| 3 |  **1c** |  **2c** | 4<br>12 | 91<br>85 |
| 4[b] | | | | |
| 5 |  **1d** |  **2d** | 4 | 95 |
| 6 |  **1e** |  **2e** | 4 | 95 |
| 7 |  **1f** |  **2f** | 4 | 94 |
| 8 |  **1g** |  **2g** | 4 | 87 |
| 9 |  **1h** |  **2h** | 4 | 81 |
| 10[c] |  **1i** |  **2i** | 12 | 12 |

[a] Isolated yield.
[b] 1 mol% PS-TBD.
[c] The reaction was carried out at 100 °C.

served when using alkyl-substituted aziridines as substrates, whereas the phenyl-substituted aziridine **1f** showed poor regioselectivity in its reactions with trimethylsilyl azide and with trimethylsilyl chloride. Although the reason for this is unclear, we suspect that electronic effects might provide a possible explanation.

**Table 3** PS-TBD-Catalyzed Ring-Opening of Aziridines with Other Silylated Nucleophilest



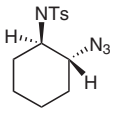
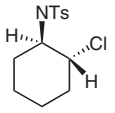
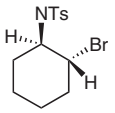
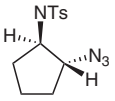
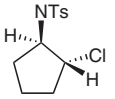
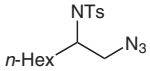
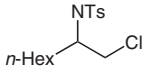
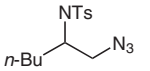
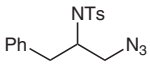
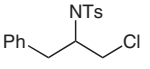
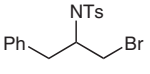
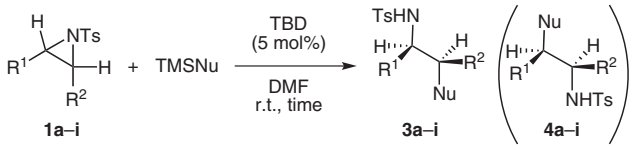
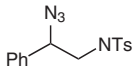
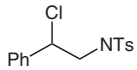
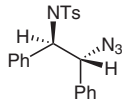
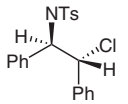

| Entry | Aziridine | Nu | Major product | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | **1a** | $N_3$ |  **3a** | 8 | 94 |
| 2 | **1a** | Cl |  **3a′** | 2 | 97 |
| 3 | **1a** | Br |  **3a″** | 2 | 97 |
| 4 | **1b** | $N_3$ |  **3b** | 12 | 88 |
| 5 | **1b** | Cl |  **3b′** | 2 | 95 |
| 6 | **1c** | $N_3$ |  **3c** | 8 | 95 |
| 7 | **1c** | Cl |  **3c′** | 2 | 90 |
| 8 | **1d** | $N_3$ |  **3d** | 8 | 82 |
| 9 | **1e** | $N_3$ |  **3e** | 8 | 92 |
| 10 | **1e** | Cl |  **3e′** | 1 | 98 |
| 11 | **1e** | Br |  **3e″** | 1 | 98 |

**Table 3** PS-TBD-Catalyzed Ring-Opening of Aziridines with Other Silylated Nucleophilest (continued)




| Entry | Aziridine | Nu | Major product | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|
| 12 | **1f** | $N_3$ |  **4f** | 12 | 97[b] |
| 13 | **1f** | Cl |  **4f′** | 2 | 91[c] |
| 14[d] | **1i** | $N_3$ |  **3i′** | 8 | 80 |
| 15[d] | **1i** | Cl |  **3i″** | 12 | 75 |

[a] Isolated yield; product **3** was obtained exclusively unless otherwise noted.
[b] Regioisomer ratio **3f**/**4f** = 22:78.
[c] Regioisomer ratio **3f′**/**4f′** = 10:90.
[d] The reaction was carried out at 30 °C.

In conclusion, we have shown that ring-opening reactions of *N*-tosylaziridines with trimethylsilyl cyanide, trimethyl azide, or trimethylsilyl halides are catalyzed by 5 mol% of PS-TBD under mild conditions. Furthermore, PS-TBD can be easily recovered and reused with minimal loss of activity after five runs. These reactions provide a simple and environmentally friendly method for the synthesis of highly functionalized β-amino acids, 1,2-diamines, or 1,3-diamines.

All reactions were performed under argon in oven-dried glassware. Flash column chromatography was performed on silica gel (Wakogel C-200). Preparative TLC was carried out on silica gel (Wakogel B-5F). Anhyd DMF, THF, toluene, and MeCN were purchased from Wako Pure Chemical Industries, Ltd. (Osaka). Other commercially available reagents were used as received without further purification. The aziridines were prepared according to a literature procedure.[13] Yields refer to isolated compounds, estimated to be >95% pure, as determined by $^1$H NMR spectroscopy. IR spectra were recorded on a Jasco FT/IR-430 spectrometer. $^1$H and $^{13}$C NMR spectra were recorded for solns in $CDCl_3$ with TMS as internal standard on a Bruker Avance III instrument. HRMS data were measured on a JEOL JMS-700 mass spectrometer.

**PS-TBD Catalyzed Ring Cleavage of Aziridines with Silylated Nucleophiles; General Procedure**

The aziridine (1.0 mmol) and the silylated nucleophile (1.25 mmol) were added to a soln of PS-TBD (0.05mmol) in DMF (1 mL) at r.t. or 80 °C. When the reaction was complete (TLC), EtOAc (5 mL) was added to the mixture and the PS-TBD was separated by filtration. The filtrate was concentrated under vacuum and purified by column chromatography [silica gel, EtOAc–hexane (1:3)] to give the corresponding product. The recovered catalyst was reusable after washing with acetone and $H_2O$, and drying in vacuo.

***N*-(*trans*-2-Cyanocyclohexyl)tosylamide (2a)**[4]

By following the general procedure, the reaction of aziridine **1a** (251 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave colorless cubes; yield: 264 mg (95%); mp 67–70 °C.

IR (KBr): 3250, 2250, 1620 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.20–1.38 (m, 3 H), 1.51–1.67 (m, 3 H), 1.86–1.94 (m, 1 H), 1.97–2.04 (m, 1 H), 2.43 (s, 3 H), 2.66 (br s, 1 H), 3.35 (dq, *J* = 4.6, 8.0 Hz, 1 H), 5.32 (d, *J* = 8.0 Hz, 1 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.80 (d, *J* = 8.5 Hz, 2 H).

$^{13}$C NMR: (125 MHz, $CDCl_3$): δ = 21.5, 22.6, 22.9, 27.1, 31.4, 34.4, 52.7, 120.2, 127.2, 129.8, 137.1, 143.9.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}N_2O_2S$: 279.1167; found: 279.1169.

***N*-(*trans*-2-Cyanocyclopentyl)tosylamide (2b)**[4]

By following the general procedure, the reaction of aziridine **1b** (237 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave colorless plates; yield: 235 mg (89%); mp 109–111 °C.

IR (KBr): 3260, 2250, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.40–1.48 (m, 1 H), 1.64–1.73 (m, 2 H), 1.74–1.85 (m, 1 H), 1.86–1.96 (m, 1 H), 2.00–2.07 (m, 1 H), 2.41 (s, 3 H), 2.83 (dt, *J* = 6.0, 8.5 Hz, 1 H), 3.69–3.75 (m, 1 H), 5.71 (d, *J* = 7.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.4, 22.6, 28.9, 32.5, 35.6, 58.6, 121.1, 127.2, 129.9, 136.5, 144.0.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{17}N_2O_2S$: 265.1011; found: 265.1021.

***N*-[1-(Cyanomethyl)heptyl]tosylamide (2c)**[4]

By following the general procedure, the reaction of aziridine **1c** (281 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave a colorless oil; yield: 257 mg (91%).

IR (neat): 3310, 2250, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.5 Hz, 3 H), 1.07–1.20 (m, 8 H), 1.47–1.58 (m, 2 H), 2.41 (s, 3 H), 2.54 (dd, *J* = 3.5, 16.5 Hz, 1 H), 2.64 (dd, *J* = 6.0, 16.5 Hz, 1 H), 3.38–3.41 (m, 1 H), 4.83 (d, *J* = 8.0 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 14.0, 21.5, 22.4, 25.0, 25.2, 28.4, 31.4, 33.9, 50.0, 116.7, 127.0, 129.9, 137.0, 144.0.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{25}N_2O_2S$: 309.1637; found: 309.1628.

***N*-[1-(Cyanomethyl)pentyl]tosylamide (2d)**[4]

By following the general procedure, the reaction of aziridine **1d** (253 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave a colorless oil; yield: 266 mg (95%).

IR (neat): 3270, 2240, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.5 Hz, 3 H), 1.08–1.24 (m, 4 H), 1.47–1.58 (m, 2 H), 2.41 (s, 3 H), 2.55 (dd, *J* = 4.0, 16.5 Hz, 1 H), 2.65 (dd, *J* = 6.0, 16.5 Hz, 1 H), 3.38–3.42 (m, 1 H), 4.80–4.83 (m, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 14.1, 21.7, 25.1, 28.8, 31.4, 33.4, 50.5, 116.6, 127.2, 129.8, 137.5, 143.9.



HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}N_2O_2S$: 281.1324; found: 281.1336.

***N*-(1-Benzyl-2-cyanoethyl)tosylamide (2e)**[5a]
By following the general procedure, the reaction of aziridine **1e** (287 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave a colorless solid; yield: 298 mg (95%); mp 90–92 °C.

IR (KBr): 3270, 2250, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 2.54 (dd, *J* = 4.0, 14.0 Hz, 1 H), 2.64 (dd, *J* = 6.0, 14.0 Hz, 1 H), 2.74 (dd, *J* = 8.0, 4.0 Hz, 1 H), 2.88 (dd, *J* = 7.5, 14.0 Hz, 1 H), 3.57–3.64 (m, 1 H), 4.82–4.88 (m, 1 H), 6.97 (d, *J* = 7.6 Hz, 2 H), 7.18–7.20 (m, 5 H), 7.53 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 24.1, 39.7, 51.3, 116.7, 126.9, 127.3, 128.9, 129.0, 129.8, 135.0, 136.3, 143.8.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}N_2O_2S$: 315.1167; found: 315.1166.

***N*-(2-Cyano-1-phenylethyl)tosylamide (2f)**[4]
By following the general procedure, the reaction of aziridine **1f** (273 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave a white solid; yield: 282 mg (94%); mp 120–122 °C.

IR (KBr): 3280, 2250, 1590 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.87 (dd, *J* = 7.0, 17.0 Hz, 1 H), 2.93 (dd, *J* = 5.0, 17.0 Hz, 1 H), 4.55 (dt, *J* = 5.5, 7.0 Hz, 1 H), 5.16 (d, *J* = 8.5 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.20–7.28 (m, 5 H), 7.65 (d, *J* = 8.5 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 26.2, 54.1, 116.3, 126.2, 127.1, 129.0, 129.2, 129.8, 136.4, 144.1.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{17}N_2O_2S$: 301.1011; found: 301.1003.

***N*-[2-Cyano-1-(4-tolyl)ethyl]tosylamide (2g)**[4]
By following the general procedure, the reaction of aziridine **1g** (287 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave a pale-yellow solid; yield: 273 mg (87%); mp 120–124 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 2.39 (s, 3 H), 2.85 (dd, *J* = 7.6, 16.8 Hz, 1 H), 2.91 (dd, *J* = 5.1, 16.8 Hz, 1 H), 4.46–4.51 (m, 1 H), 5.32 (d, *J* = 6.9 Hz, 1 H), 6.98 (d, *J* = 8.2 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.2 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.0, 21.5, 26.2, 53.9, 116.5, 126.1, 127.1, 129.7, 129.8, 134.2, 139.0, 144.0.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}N_2O_2S$: 315.1167; found: 315.1152.

***N*-[1-(4-Chlorophenyl)-2-cyanoethyl]tosylamide (2h)**[4]
By following the general procedure, the reaction of aziridine **1h** (307 mg, 1 mmol) with TMSCN (167 μL, 1.25 mmol) gave a white solid; yield: 270 mg (81%); mp 110–112 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 2.82 (dd, *J* = 7.0, 16.8 Hz, 1 H), 2.88 (dd, *J* = 5.8, 16.8 Hz, 1 H), 4.56 (dd, *J* = 7.1, 7.2 Hz, 1 H), 5.70 (d, *J* = 7.6 Hz, 1 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8.5 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 26.2, 53.5, 116.2, 127.1, 127.7, 129.2, 129.8, 134.8, 135.6, 144.2.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}ClN_2O_2S$: 334.0543; found: 334.0565.

***N*-(-2-Cyano-1,2-diphenylethyl)tosylamide (2i)**[5a]
By following the general procedure, the reaction of aziridine **1i** (175 mg, 0.5 mmol) with TMSCN (83 μL, 0.63 mmol) gave a white solid; yield: 45 mg (12%); mp 78–80 °C.

IR (KBr): 3270, 2960, 2100, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 4.27 (s, 1 H), 4.98 (br s, 1 H), 7.02 (d, *J* = 7.6 Hz, 2 H), 7.07–7.13 (m, 3 H), 7.25–7.42 (m, 7 H), 7.81 (d, *J* = 7.6 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.4, 70.1, 126.4, 127.3, 127.4, 127.7, 128.1, 128.4, 129.3, 135.4, 136.9, 137.0, 142.9.

Anal. Calcd for $C_{22}H_{20}N_2O_2S$: C, 70.19; H, 5.35; N, 7.44. Found: C, 69.90; H, 5.20; N, 7.79.

***N*-(*trans*-2-Azidocyclohexyl)tosylamide (3a)**[4]
By following the general procedure, the reaction of aziridine **1a** (251 mg, 1 mmol) with $TMSN_3$ (166 μL, 1.25 mmol) gave a colorless oil; yield: 277 mg (94%).

IR (KBr): 3300, 2940, 2090, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.12–1.33 (m, 4 H), 1.54–1.68 (m, 2 H), 1.92–2.00 (m, 2 H), 2.39 (s, 3 H), 2.91–2.95 (m, 1 H), 3.07–3.10 (m, 1 H), 5.29 (d, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 23.6, 23.8, 30.2, 32.4, 56.7, 63.5, 127.0, 129.5, 137.5, 143.3.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{19}N_4O_2S$: 295.1229; found: 295.1235.

***N*-(*trans*-2-Chlorocyclohexyl)tosylamide (3a′)**[4]
By following the general procedure, the reaction of aziridine **1a** (251 mg, 1 mmol) with TMSCl (159 μL, 1.25 mmol) gave a colorless solid; yield: 278 mg (97%); mp 98–100 °C.

IR (KBr): 3270, 2860, 1920, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.22–1.28 (m, 3 H), 1.55–1.67 (m, 3 H), 2.10–2.15 (m, 2 H), 2.39 (s, 3 H), 3.05–3.10 (m, 1 H), 3.66–3.69 (m, 1 H), 5.20 (d, *J* = 6.0 Hz, 1 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 23.4, 24.3, 32.4, 34.9, 58.7, 62.1, 127.3, 129.6, 137.2, 143.4.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{19}ClNO_2S$: 288.0825; found: 288.0833.

***N*-(*trans*-2-Bromocyclohexyl)tosylamide (3a′′)**[4]
By following the general procedure, the reaction of aziridine **1a** (251 mg, 1 mmol) with TMSBr (165 μL, 1.25 mmol) gave a white solid; yield: 321 mg (97%); mp 78–80 °C.

IR (KBr): 3270, 2870, 1900, 1610 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.23–1.30 (m, 3 H), 1.58–1.64 (m, 2 H), 1.71–1.79 (m, 1 H), 2.18–2.28 (m, 2 H), 2.40 (s, 3 H), 3.14–3.19 (m, 1 H), 3.80–3.88 (m, 1 H), 5.11 (d, *J* = 5.5 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 23.4, 25.3, 32.8, 35.7, 55.0, 58.6, 127.3, 129.6, 137.1, 143.5.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{19}BrNO_2S$: 332.0320; found: 332.0323.

***N*-(*trans*-2-Azidocyclopentyl)tosylamide (3b)**[4]
By following the general procedure, the reaction of aziridine **1b** (237 mg, 1 mmol) with $TMSN_3$ (166 μL, 1.25 mmol) gave a colorless oil; yield: 246 mg (88%).

IR (KBr): 3260, 2960, 2100, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.31–1.39 (m, 1 H), 1.51–1.65 (m, 3 H), 1.81–1.92 (m, 2 H), 2.40 (s, 3 H), 3.36 (dt, *J* = 5.0, 7.0 Hz, 1 H), 3.65–3.71 (m, 1 H), 5.54 (d, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.8, 21.5, 26.9, 29.0, 30.8, 59.7, 66.9, 126.7, 129.6, 137.0, 143.5.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{17}N_4O_2S$: 281.1072; found: 281.1075.

***N*-(*trans*-2-Chlorocyclopentyl)tosylamide (3b′)**[4]
By following the general procedure, the reaction of aziridine **1b** (237 mg, 1 mmol) with TMSCl (159 μL, 1.25 mmol) gave a colorless solid; yield: 278 mg (97%); mp 88–90 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.37–1.50 (m, 2 H), 1.66–1.78 (m, 2 H), 2.04–2.13 (m, 2 H), 2.39 (s, 3 H), 3.53–3.57 (m, 1 H), 4.01–4.12 (m, 1 H), 5.64–5.71 (br s, 1 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 20.7, 21.4, 30.3, 33.3, 62.6, 63.6, 127.1, 129.7, 137.0, 143.5.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{17}ClNO_2S$: 274.0669; found: 274.0681.

***N*-[1-(Azidomethyl)heptyl]tosylamide (3c)**[4]
By following the general procedure, the reaction of aziridine **1c** (281 mg, 1 mmol) with $TMSN_3$ (166 μL, 1.25 mmol) gave a pale-yellow oil; yield: 308 mg (95%).

IR (neat): 3280, 2940, 2100, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.0 Hz, 3 H), 1.10–1.50 (m, 10 H), 2.41 (s, 3 H), 3.26–3.30 (m, 3 H), 4.80 (d, *J* = 7.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 14.0, 21.5, 22.4, 25.3, 28.8, 31.6, 32.6, 53.2, 55.0, 127.0, 129.7, 137.7, 143.6.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}N_4O_2S$: 325.1698; found: 325.1698.

***N*-[1-(Chloromethyl)heptyl]tosylamide (3c′)**[4]
By following the general procedure, the reaction of aziridine **1c** (281 mg, 1 mmol) with TMSCl (159 μL, 1.25 mmol) gave a colorless oil; yield: 285 mg (90%).

IR (neat): 3280, 2840, 1610 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.5 Hz, 3 H), 1.10–1.25 (m, 8 H), 1.39–1.47 (m, 1 H), 1.51–1.57 (m, 1 H), 2.40 (s, 3 H), 3.40–3.52 (m, 3 H), 4.91 (d, *J* = 8.5 Hz, m, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 14.0, 21.5, 22.4, 225, 25.2, 28.7, 31.4, 32.3, 48.1, 53.8, 127.0, 129.7, 137.8, 143.6.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}ClNO_2S$: 318.1295; found: 318.1301.

***N*-[1-(Azidomethyl)pentyl]tosylamide (3d)**[4]
By following the general procedure, the reaction of aziridine **1d** (253 mg, 1 mmol) with $TMSN_3$ (166 μL, 1.25 mmol) gave a colorless oil; yield: 243 mg (82%).

IR (neat): 3280, 2100, 1600 cm$^{-1}$.

$^1$H NMR: (500 MHz, $CDCl_3$): δ = 0.74 (t, *J* = 7.0 Hz, 3 H), 1.04–1.50 (m, 6 H), 2.40 (s, 3 H), 3.24–3.29 (m, 3 H), 5.00 (br s, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 13.7, 21.5, 22.1, 27.5, 32.2, 53.2, 54.9, 126.9, 129.6, 137.6, 143.4.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{21}N_4O_2S$: 297.1385; found: 297.1386.

***N*-(2-Azido-1-benzylethyl)tosylamide (3e)**[6]
By following the general procedure, the reaction of aziridine **1e** (287 mg, 1 mmol) with $TMSN_3$ (166 μL, 1.25 mmol) gave a colorless oil; yield: 304 mg (92%).

IR (neat): 3270, 2090, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.68 (dd, *J* = 7.0, 14.0 Hz, 1 H), 2.75 (dd, *J* = 7.5, 14.0 Hz, 1 H), 3.28 (dd, *J* = 4.0, 12.0 Hz, 1 H), 3.31 (dd, *J* = 6.5, 12.0 Hz, 1 H), 3.45–3.54 (m, 1 H), 4.92 (d, *J* = 8.0 Hz, 1 H), 6.98 (d, *J* = 8.5 Hz, 2 H), 7.10–7.35 (m, 5 H), 7.60 (d, *J* = 8.5 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 38.4, 53.7, 54.3, 126.8, 127.2, 128.6, 128.7, 129.1, 129.6, 136.1, 136.7, 143.4.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}N_4O_2S$: 331.1229; found: 331.1236.

***N*-(1-Benzyl-2-chloroethyl)tosylamide (3e′)**[6]
By following the general procedure, the reaction of aziridine **1e** (287 mg, 1 mmol) with TMSCl (159 μL, 1.25 mmol) gave a colorless oil; yield: 316 mg (98%).

IR (neat): 3270, 2890, 1600 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 2.75 (dd, *J* = 6.5, 13.5 Hz, 1 H), 2.87 (dd, *J* = 7.5, 13.5 Hz, 1 H), 3.43 (dd, *J* = 5.5, 11.5 Hz, 1 H), 3.47 (dd, *J* = 3.0, 11.5 Hz, 1 H), 3.64–3.71 (m, 1 H), 4.88 (d, *J* = 7.0 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 2 H), 7.17–7.22 (m, 5 H), 7.61 (d, *J* = 8.5 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.5, 38.2, 46.8, 55.1, 126.9, 127.0, 128.7, 128.8, 129.1, 129.7, 136.1, 137.2, 143.5.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}ClNO_2S$: 324.0825; found: 324.0830.

***N*-(1-Benzyl-2-bromoethyl)tosylamide (3e″)**[6]
By following the general procedure, the reaction of aziridine **1e** (287 mg, 1 mmol) with TMSBr (165 μL, 1.25 mmol) gave a white solid; yield: 360 mg (98%); mp 32–34 °C.

IR (KBr): 3250, 2850, 1590 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 2.73 (dd, *J* = 5.5, 14.0 Hz, 1 H), 2.87 (dd, *J* = 8.0, 14.0 Hz, 1 H), 3.31 (dd, *J* = 5.5, 11.0 Hz, 1 H), 3.34 (dd, *J* = 5.0, 11.0 Hz, 1 H), 3.57–3.62 (m, 1 H), 5.02 (d, *J* = 8.0 Hz, 1 H), 7.01–7.08 (m, 2 H), 7.15–7.22 (m, 5 H), 7.62 (d, *J* = 8.5 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.4, 37.4, 41.1, 54.6, 126.9, 127.0, 128.6, 129.1, 129.5, 129.8, 136.0, 137.1, 143.4.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}BrNO_2S$: 368.0320; found: 368.0318.

***N*-(2-Azido-2-phenylethyl)tosylamide (4f)**[4] **and *N*-(2-Azido-1-phenylethyl)tosylamide (3f)**
By following the general procedure, the reaction of aziridine **1f** (273 mg, 1 mmol) with $TMSN_3$ (166 μL, 1.25 mmol) gave a white solid; yield: 306 mg (97%, 78:22 mixture of regioisomers **4f** and **3f**).

IR (KBr): 3280, 2100, 1590 cm$^{-1}$.

$^1$H NMR (500 MHz, $CDCl_3$): δ (**4f**) = 2.43 (s, 3 H), 3.06 (ddd, *J* = 5.0, 8.0, 13.5 Hz, 1 H), 3.21 (ddd, *J* = 5.0, 7.5, 13.5 Hz, 1 H), 4.60 (dd, *J* = 5.5, 9.0 Hz, 1 H), 5.11 (dd, *J* = 5.5, 7.5 Hz, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.18–7.38 (m, 5 H), 7.72 (d, *J* = 8.0 Hz, 2 H); δ (**3f**) = 2.37 (s, 3 H), 3.53 (d, *J* = 6.5 Hz, 2 H), 4.47 (dd, *J* = 6.0, 16.5 Hz, 1 H), 5.62 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.18–7.38 (m, 5 H), 7.60 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ (**4f**) = 21.5, 48.0, 65.4, 126.9, 127.0, 128.9, 129.0, 129.8, 136.2, 136.7, 143.7; δ (**3f**) = 21.4, 55.9, 57.1, 126.7, 127.0, 128.1, 128.6, 129.4, 137.0, 137.5, 143.4.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{17}N_4O_2S$: 317.1072; found: 317.1075 (mixture of regioisomers **4f** and **3f**).

***N*-(2-Chloro-2-phenylethyl)tosylamide (4f′)**[4] **and *N*-(2-Chloro-1-phenylethyl)tosylamide (3f′)**
By following the general procedure, the reaction of aziridine **1f** (273 mg, 1 mmol) with TMSCl (159 μL, 1.25 mmol) gave a white solid; yield: 281 mg (91%; 90:10 mixture of regioisomers **4f′** and **3f′**); mp 62–65 °C.

IR (KBr): 3260, 2100, 1600 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ (**4f′**) = 2.41 (s, 3 H), 3.36–3.47 (m, 2 H), 4.86 (dd, *J* = 6.1, 8.2 Hz, 1 H), 5.20 (dd, *J* = 6.5, 6.7 Hz, 1 H), 7.28–7.32 (m, 7 H), 7.71 (d, *J* = 8.3 Hz, 2 H); δ (**3f′**) = 2.39 (s, 3 H),

3.67 (dd, *J* = 5.8, 11.4 Hz, 1 H), 3.71 (dd, *J* = 6.4, 11.4 Hz, 1 H), 4.55 (q, *J* = 6.7 Hz, 1 H), 5.39 (t, *J* = 6.6 Hz, 1 H), 7.25–7.35 (m, 7 H), 7.59 (d, *J* = 8.3 Hz, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ (**4f′**) = 21.4, 50.2, 61.6, 126.9, 127.1, 128.8, 128.9, 129.7, 136.9, 137.8, 143.6; δ (**3f′**) = 21.4, 47.8, 58.4, 126.8, 127.0, 128.5, 128.7, 129.7, 136.4, 137.3, 143.5.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{17}ClNO_2S$: 310.0669; found: 310.0655 (mixture of regioisomers **4f′** and **3f′**).

***N*-(-2-Azido-1,2-diphenylethyl)tosylamide (3i′)**[5e]
By following the general procedure, the reaction of aziridine **1i** (175 mg, 0.5 mmol) with $TMSN_3$ (83 μL, 0.63 mmol) gave a white solid; yield: 157 mg (80%); mp 62–65 °C.

IR (KBr): 3270, 2960, 2100, 1600 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 4.48–4.51 (m, 1 H), 4.69 (d, *J* = 6.5 Hz, 1 H), 5.53 (br s, 1 H), 6.94 (d, *J* = 7.0 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 7.05–7.15 (m, 5 H), 7.20–7.24 (m, 3 H), 7.38 (d, *J* = 8.0 Hz, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.4, 62.3, 70.2, 126.9, 127.4, 127.5, 127.8, 128.1, 128.6, 129.2, 135.4, 136.9, 137.0, 143.0.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}N_4O_2S$: 393.1385; found: 393.1377.

***N*-(-2-Chloro-1,2-diphenylethyl)tosylamide (3i″)**
By following the general procedure, the reaction of aziridine **1i** (175 mg, 0.5 mmol) with TMSCl (80 μL, 0.63 mmol) gave product **3i″** as a white solid; yield: 144 mg (97%); mp 72–74 °C.

IR (KBr): 3250, 2960, 2880, 1600 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 4.72 (t, *J* = 6.5 Hz, 1 H), 5.00 (d, *J* = 6.5 Hz, 1 H), 5.39 (d, *J* = 6.0 Hz, 1 H), 6.90 (d, *J* = 7.0 Hz, 2 H), 7.02–7.06 (m, 4 H), 7.08–7.15 (m, 2 H), 7.16–7.21 (m, 4 H), 7.38 (d, *J* = 7.0 Hz, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.5, 63.8, 66.8, 127.1, 127.9, 128.0, 128.3, 128.7, 129.2, 136.5, 136.9, 136.9, 143.2.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}ClNO_2S$: 386.0982; found: 386.0988.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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